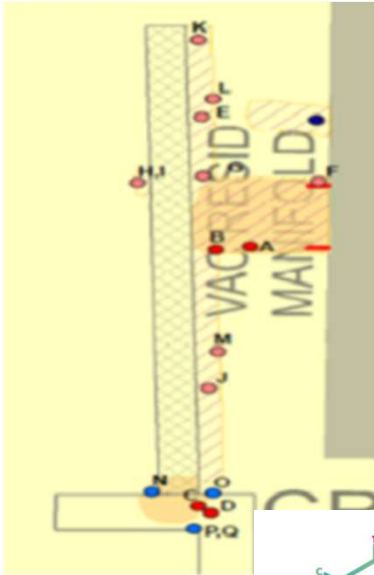


## Discerning recent and historical spill material using European Standard EN 15522-2:2023

- Detlef Birkholz,<sup>1</sup> Roger Hodges,<sup>2</sup> Mike Morden,<sup>2</sup> Laurie Hammond,<sup>3</sup>

- **1. D.A. Birkholz, Analytical Consultant, Inc.**
  - **2. Gibson Energy**
  - **3. WSP E & I Canada**



Forensic services in toxicology, chemistry biology sampling & statistics

Refineries are sold and often redeveloped by their buyers. The new owners may redevelop the site to refine and sell differing petroleum products than the original owners. Redevelopment requires a provincial permit. Contamination discovered on the site has to be identified and the source promulgated. New owners are may not be required to cleanup petroleum identified as “historical”. In other words petroleum released to the environment by previous owners. However, petroleum releases by the new owners have to be mitigated in order to receive redevelopment permits.

## Background

- Leak from branch of pipe connected to 3-Phase separator but no longer in use (not flowing)
- Investigation into extent of spill
- Sample taken from operational 3-Phase separator
- Spill material collected from one site following soil excavation (i.e. spill product and water mixture 'Gasoline Leak Sample')
- Soil samples collected from a number of sites where soil staining was observed
- All samples analyzed for petroleum hydrocarbons following CCME guidelines (i.e. BTEX AND PHC F1-F4 hydrocarbons)
- Review of PHC data resulted in the identification of sites of interest for further forensic testing using method EN 15522-2:2023



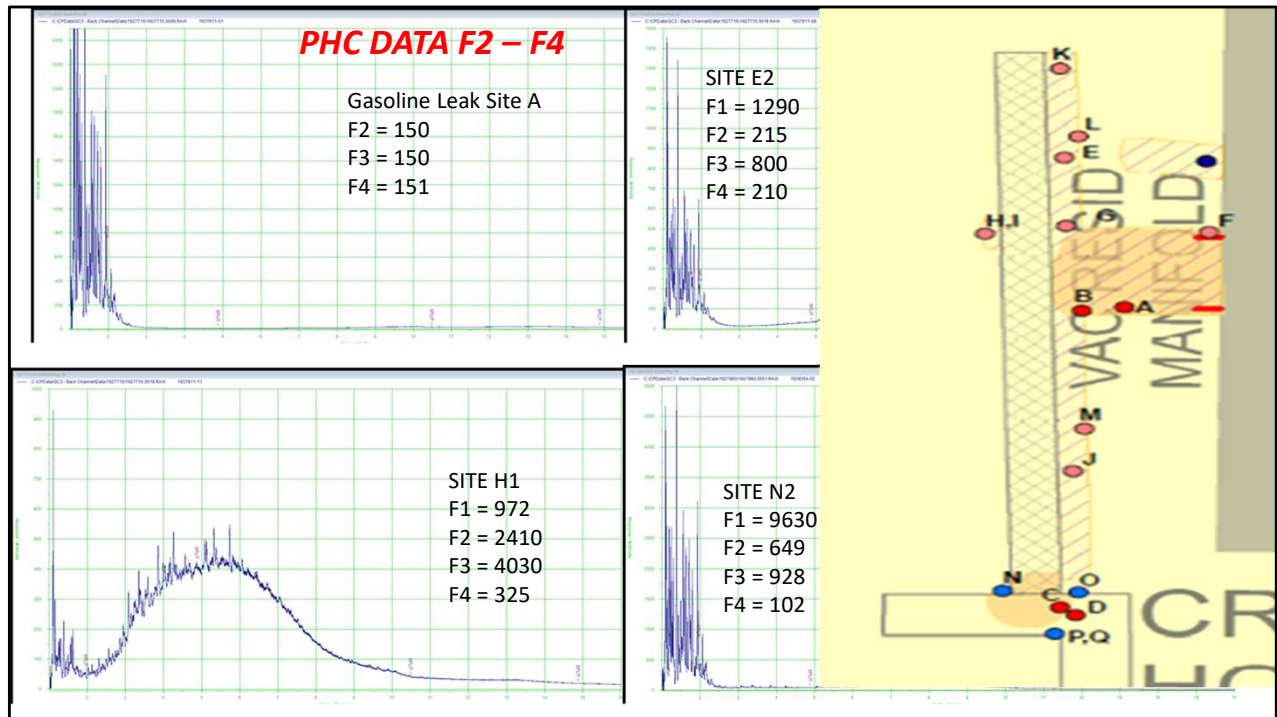
Excavation of a former refinery, for the purposes of redevelopment discovered a leak in the vicinity of a pipe which at one time was connected to a 3-phase separator. However, there was no observed flow through this pipe. An investigation was performed to determine the extent of the spill material. Samples of product were taken from the three phase separator, as well as LNAPL discovered on the site. Soil samples were collected from a number of sites where “soil staining” was observed. All samples, LNAPL and soil, were subjected to PHC analyses (BTEX, F1-F4) following CCME guidelines. Review of data obtained resulted in the identification of sites requiring further analyses.

## Why Forensics

- Differentiation between historical releases and any current releases required.
- Eras of ownership can mean eras of differential liability.
- Forensics key for understanding of liability associated with areas of any future operational expansion
- EN2023 method ideally suited for this task.
- Ref: EN 15522-2:2023. Oil spill identification – Petroleum and petroleum related products – Part 2: Analytical method and interpretation of results based on GC-FID and GC-low resolution – MS analyses. Available European Committee for Standardization, CEN-CENELEC Management Centre, Rue de la Science 23, B1040 Brussels



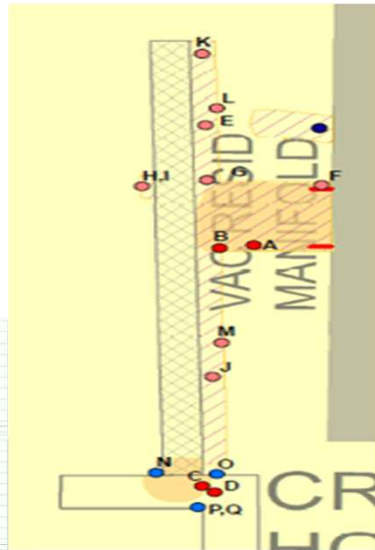
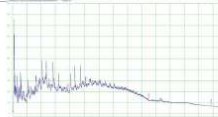
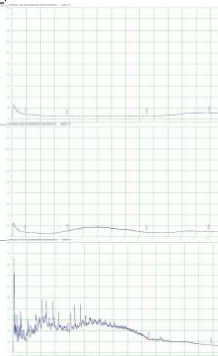
Differentiation of of petroleum contamination on this site was critical to determining source of petroleum hydrocarbons, especially those associated with present and past operations (i.e. historical releases). Method EN 2023, developed by the oil spill international network of experts, (OSINET) was ideally suited for this task. The method applies to a wide variety of petroleum products and has been subject to extensive peer review as well as interlaboratory study by organizations around the world.



Three sites were identified for further study following review of the PHC data: Sites A, E2, H1, and N2. Chromatograms pertain to PHC – F2 – F4. Chromatograms for A, E2, and N2 appear similar indicating straight run gasoline. Chromatograms for H1 is different indicating heavier petroleum product.

## PHC Data and Chromatograms for sites K, P and Q

ID	Depth from soil surface (m)	Depth from top of sidewalk (m)	Colour	Benzene	Ethylbenzene	Toluene	Xylenes, total	F1 (C6-C10)	F2 (C10-C16)	F3 (C16-C34)	F4 (C34-C50)	Forensic candidate
K1	0.05	0.50	brown	<0.02	<0.05	<0.05	<0.05	<7	<4	<8	<6	
K2	0.10	0.55	slight st	<0.02	<0.05	<0.05	<0.05	9	14	151	<6	
P1, Q1 duplicates	0.10	0.71	brown v	1	7	0.44	3	456	628	1,160	299	



Area of investigation bordered by site K and P,Q. Note minimal hydrocarbons detected at these sites, i.e. area of release was well defined

## OSINET Forensic Methods

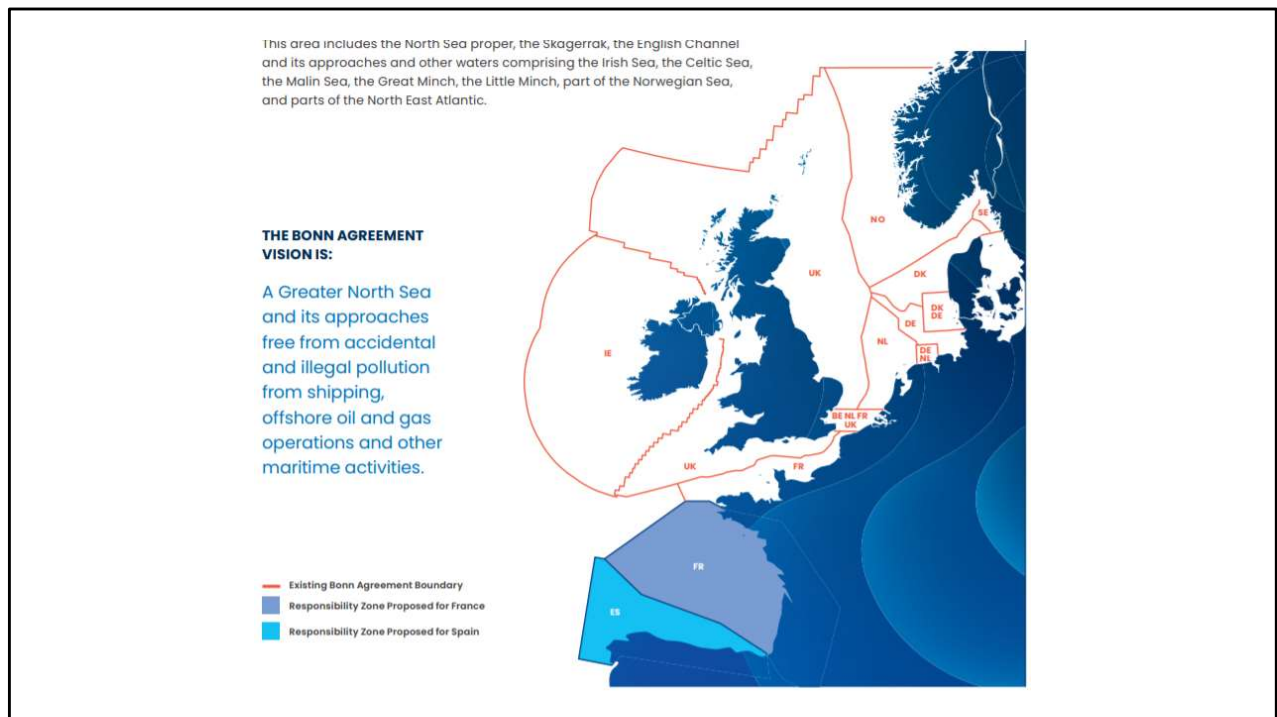
- Bonn Agreement formulated in 2005 and network of expert chemists established specializing in oil spill identification techniques, now known as OSINET (oil spill identification, network).
- Bonn-OSINET was initiated with the objective to improve the quality of the laboratories and to stimulate cooperation and mutual assistance

### ***History of OSINET Analytical Methods:***

- Since 1991, the Nordtest method for oil spill identification (Nordtest, 1991) has formed an important forensic “platform” in relation to oil spill identification, not only in the Scandinavian countries, but also in other European countries following its recommendation in and adoption by the Bonn Agreement *Counter Pollution Manual*.
  - CEN Technical Report, 2006
  - CEN Technical Report, 15522-2: 2012
    - EN 15522-2: 2023

Method EN 15522-2:2023 was broadened to include light hydrocarbons such as naphtha and expanded analytes for diesel products.

Ref: Lunderberg, R. (2019). Validation of biomarkers for the revision of the CEN/TR 15522-2:2012 method. A statistical study of sampling, discrimination powers and weathering of new biomarkers for comparative analysis of lighter oils. Linkopings university, Department of Physics, Chemistry and Biology, ISRN: LITH-IFM-G-EX-19/3681-SE



OSINET (oil spill international network of expert) was formed in 2005 in response to the Tricolor spill. In 2005 the Bonn Agreement requested laboratories of countries around the North Sea to improve their cooperation, promulgated by problems that occurred during the Tricolor incident (2002) in the British Canal. Each country participating in the Bonn Agreement assigned a laboratory to be responsible for the oil spill cases in their area, and at a meeting of national lab representatives in Ostend (Be), the Bonn-Oil Spill Identification Network of experts (Bonn-OSINet, 2005) was formed (Dahlmann and Kienhuis, 2015). Bonn-OSINet was initiated with the objective to improve the quality of the laboratories and to stimulate cooperation and mutual assistance.



### *Operating Principals of OSINET*

- Forensic research on the selection of appropriate chemicals and ratios to identify and measure in relation to spills of differing petroleum products. Dates back to 2002.
- Perform international round robin studies annually applying suggested measurements. Annually since 2002. Now every two years because too many labs to evaluate.
- Perform statistical analyses and determine diagnostic power of chemical ratios.
- Those chemical ratios with high diagnostic power are deemed normative.
- Those with good, but lower diagnostic power deemed informative.
- Continuing research and interlaboratory studies. Method EN2023 light petroleum products are being dealt with (e.g. condensates).
- Website dedicated to OSINET members sharing observations, publications, and findings.
- Currently there are ***44 laboratories associated with 26 countries*** (2017 report).
- Forensic data is shared on a global basis using COSIWEB in order to identify spill material globally.
- Currently 6 Canadian Labs are OSINET members 4-Federal (Environment Canada), 2- private.
- Currently 3 US Labs are OSINET members all private

This slide is self explanatory



## Daubert Standard

- **Daubert standard** is a [rule of evidence](#) regarding the admissibility of [expert witness testimony](#). Pursuant to Rule 104(a), in *Daubert* the U.S. Supreme Court suggested that the following factors be considered:<sup>[28]</sup>
  - Has the technique been tested in actual field conditions (and not just in a laboratory)?
  - Has the technique been subject to peer review and publication?
  - What is the known or potential rate of error?
  - Do standards exist for the control of the technique's operation?
  - Has the technique been generally accepted within the relevant scientific community?
  - Canadian Supreme Court “did list a number of factors that could be helpful in evaluating the soundness of novel science.”
  - It is too early to say *Daubert*-like rules are likely to be applied in Canada in the near future. But Canadian class certification courts are starting to exercise an important evidentiary gatekeeping role (*Barry Glaspell* (bglaspell@blg.com) is a senior class action counsel at *Borden Ladner Gervais LLP*,).

Daubert standard refers to a U.S. Federal ruling. Most spill incidents are dealt with under state and or provincial statutes unless spill impacts multiple borders (states/provinces). Canadian Federal Court has used this in one Federal case but not accepted carte blanche. Not all US states have adopted the Daubert Standard. Standard goes well beyond just peer review. Of the five critical factors EN2023 meets all requirements. Technique accepted around the world: 44 laboratories operating in 26 countries (2017 data). New labs operating in new countries have been added.

## ANALYTICAL METHODS – Petroleum Products

- An aliquot ( $500 \pm 5$  mg) of each product (Gasoline Leak and 3-Phase Separator gas) was weighed into a 12 mL vial and diluted to 5 mL with pentane. The mixture was placed in a freezer for 1 h to facilitate asphaltene precipitation. No precipitate was observed and therefore 200  $\mu$ L of each pentane solution was diluted to 1 mL with dichloromethane solvent and analyzed.

Slide is self explanatory

## SOIL SAMPLES

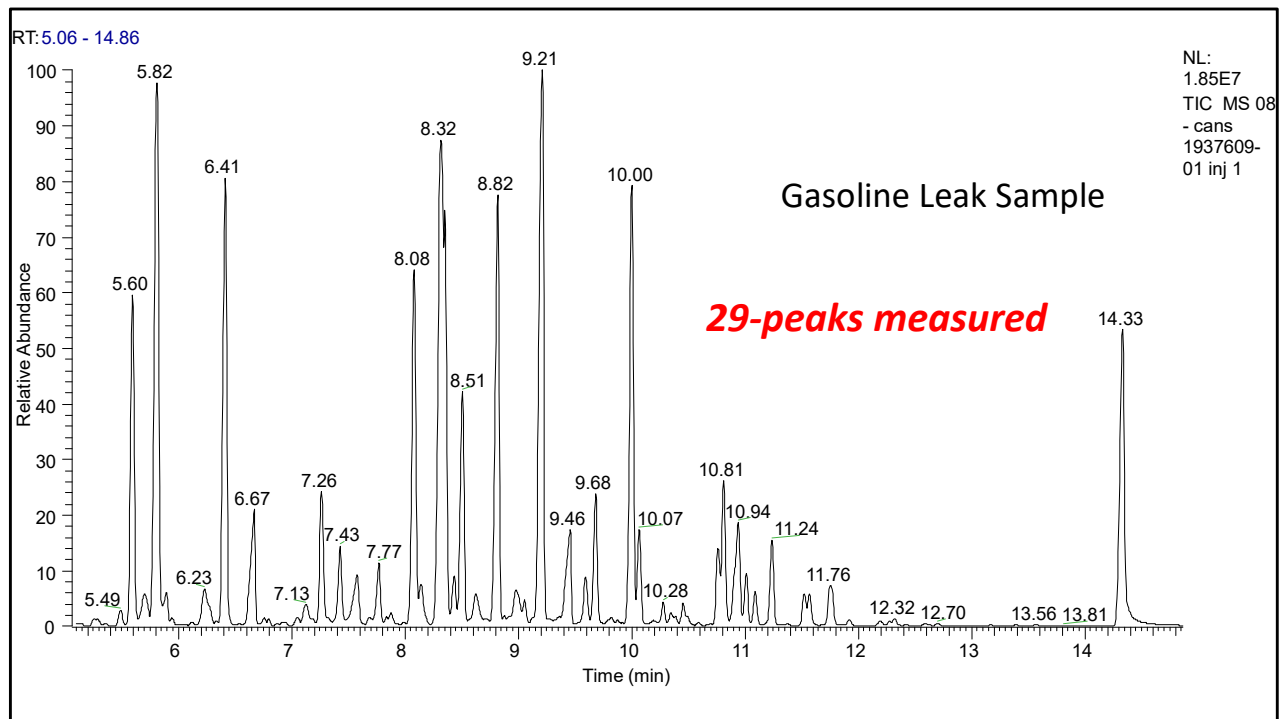
- An aliquot (based upon soil PHC data) of soil was weighed into a new 1 quart new galvanized paint can as follows:
  - (E2) – 44.5 g
  - (H1) – 14.5 g
  - (N2) – 12.1 g
- An aliquot of each liquid product (100  $\mu$ L) was added to a Kimwipe and placed inside a new 1 quart galvanized paint can. Following the addition of 638 micrograms ( $\mu$ g) of surrogate (naphthalene-d8), along with a carbon strip (attached via a paper clip held to the lid of the paint can with a rare earth magnet) the cans were sealed and placed in an oven maintained at 70°C for 24h.
- Soil samples required addition of surrogate and carbon strip. Processed as above.
- Following heat treatment, the cans were removed from the oven, allowed to equilibrate to room temperature and opened. The carbon strip was removed and placed into a 1 mL gas chromatographic vial. Carbon disulphide, 600  $\mu$ L, was added to the vial containing the carbon strip. This solvent contained an internal standard, namely undecane-d24, at a concentration of 0.404 mg/mL.

Slide is self explanatory

## Chemical Analyses

- Chemical analyses were performed using gas chromatography/mass spectrometry (GC/MS) using EN2023. The main difference from the previous method CEN/TR 15522-2:2012, is that the method is extended to light petroleum hydrocarbons such as condensate samples by including a range of low boiling compounds.
- Analyses were performed in a single batch and contained 3 - 2016 composite LNAPL samples taken from another site as a reference oil (mixture of condensate and crude oil). The 2016 LNAPL was used as a template to correctly identify petroleum biomarkers. All samples were analyzed in duplicate.
- All headspace samples were analyzed split 20:1. Liquid product samples were analyzed splitless.
- It is important to point out that oil samples can be stored indefinitely if stored at temperatures from above freezing to 30°C (NOAA, 2011). Paracel Laboratories stored 2016 LNAPL as well as the samples listed in Table 1 in a refrigerator maintained at 5°C.

Slide is self explanatory



This is a gas chromatography/mass spectrometry total ion chromatogram. Note the retention times shown. These are consistent and used as peak identifiers. Gasoline leak is liquid product on water collected by refinery staff. It may have sat in the dead end pipe a long time and be from different distillation of a different crude than represented by the 3phase separator sample.

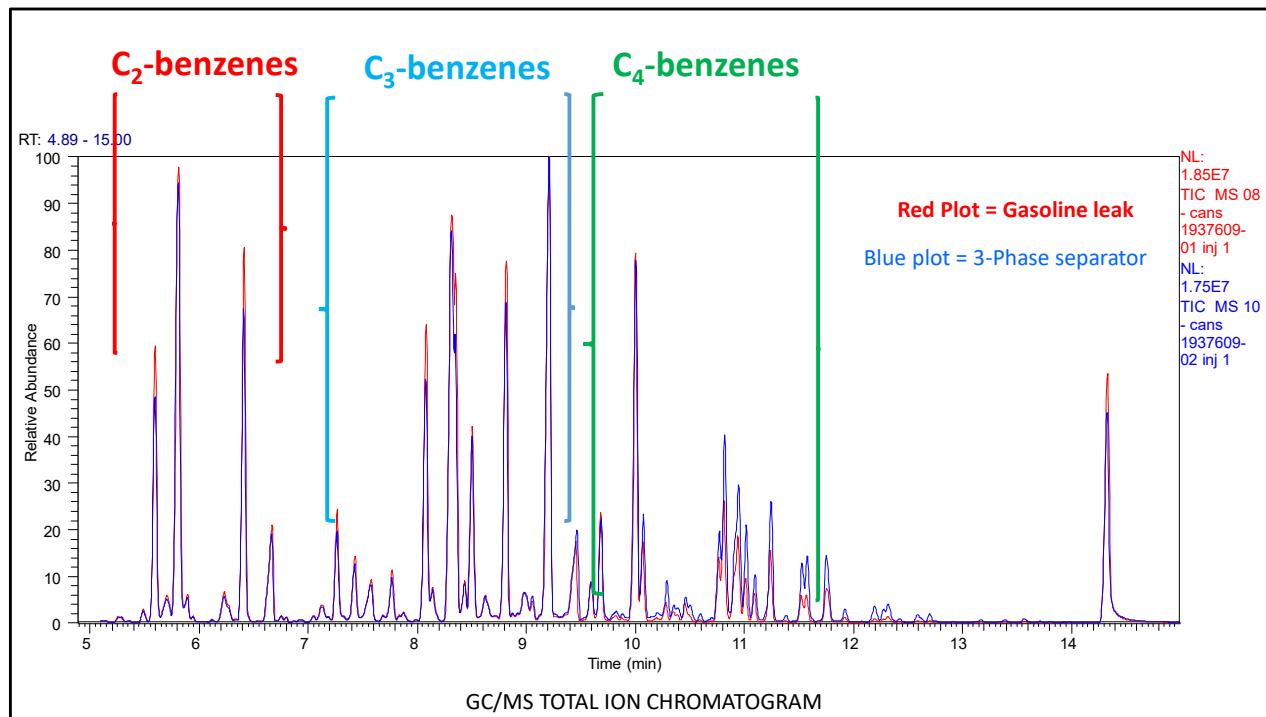
## Chemometrics

- GC/MS TIC data subjected to Atichison transformation
- Principal components analysis (PCA) performed using XLSTAT
- Score plots subjected to Agglomerative hierarchical clustering
- Dissimilarity: Euclidean distance (Ward's method)
- Dissimilarity: Mahalanobis distance (unweighted pair group average)

ATICHISON TRANSORMATIONS INVOLVES NORMALIZATION TO THE GEOMETRIC MEAN. THIS DATA IS THEN SUBJECTED TO NATURAL LOG TRANSFORMATION.

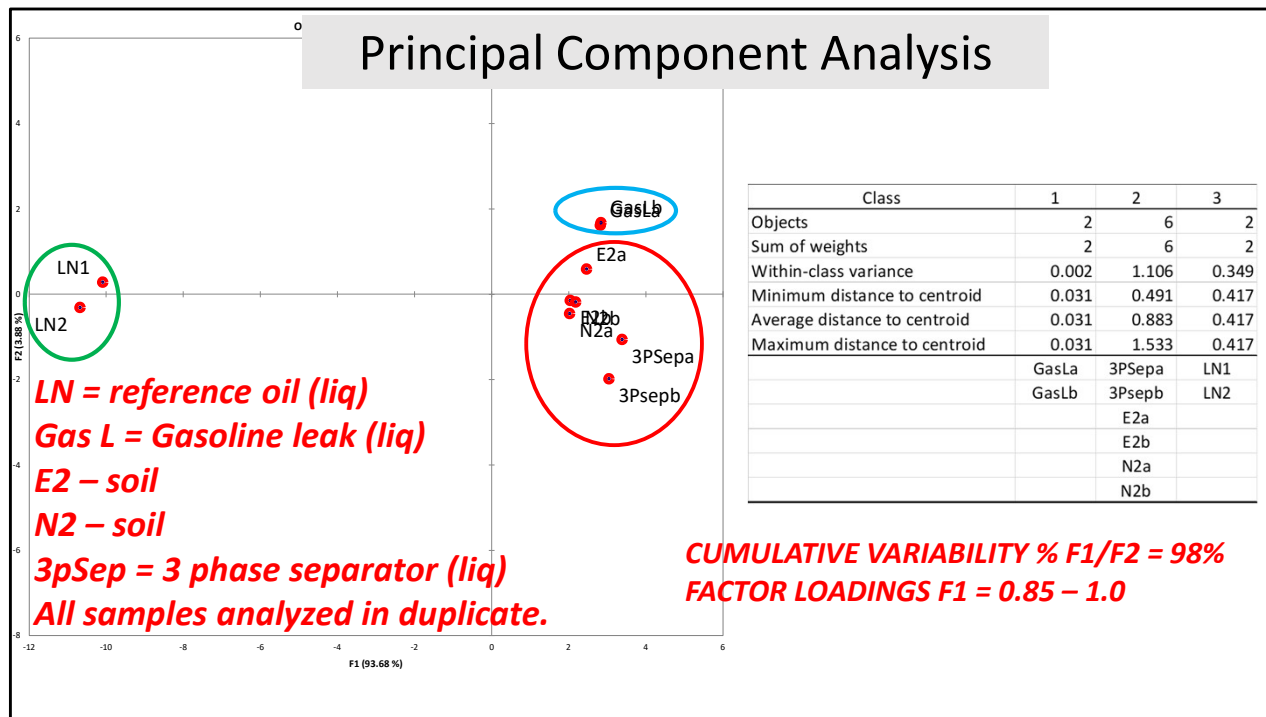
PCA DOES PERFORM CORRELATION ANALYSIS

FURTHER CORRELATIONS ARE PERFORMED USING THE PCA DATA (FACTOR SCORES) AND SUBJECTING THEM TO CLUSTER ANALYSIS TO DETERMINE WHICH SAMPLES ARE MOST SIMILAR TO EACH OTHER. BOTH EUCLIDEAN DISTANCE AND MAHALANOBIS DISTANCE WERE EMPLOYED FOR THE CLUSTER ANALYSIS

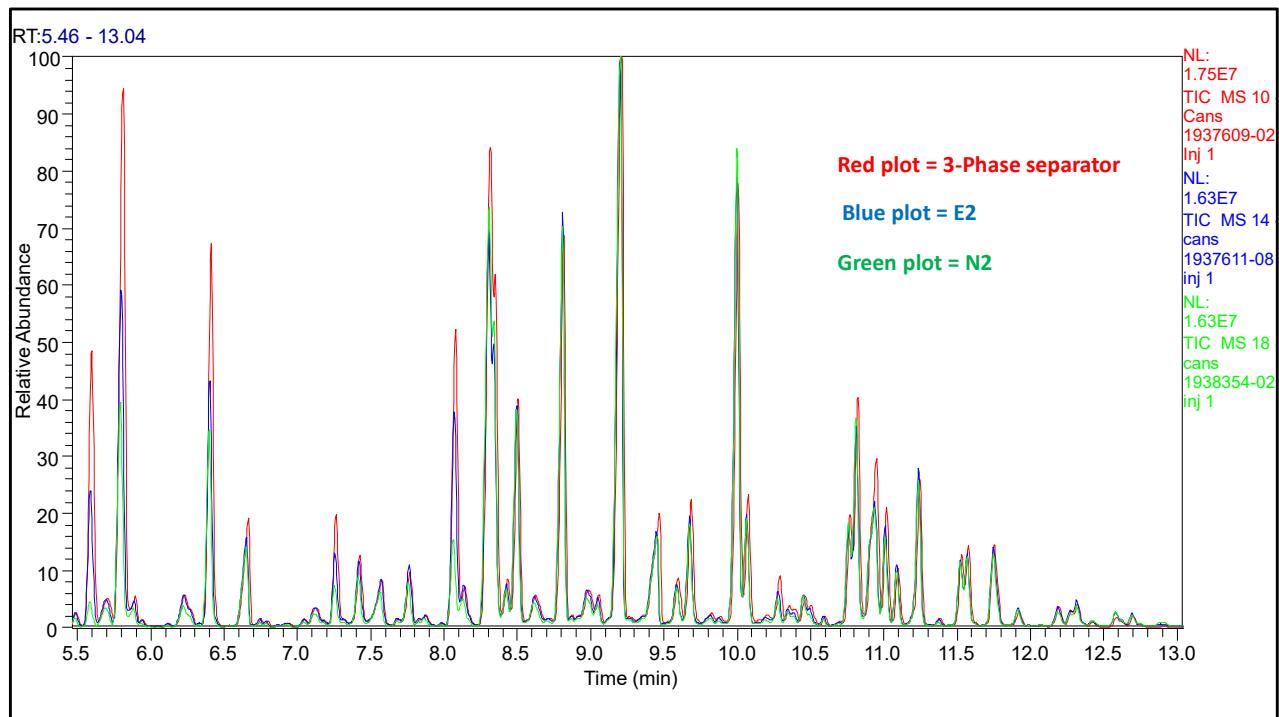


THIS SLIDE SHOWS THE GC/MS TIC OBSERVED FOR THE GASOLINE LEAK NAD 3PHASE SEPARATOR SAMPLE. IT IS OBSERVED THAT THE MAJORITY OF COMPOUNDS DETECTED USING GC/MS TOTAL ION CHROMATOGRAM ARE ALKYLATED BENZENES. THE C<sub>4</sub>-BENZENES ARE PARTICULARLY IMPORTANT BECAUSE THEY HAVE BEEN USED IN ARSON INVESTIGATIONS WHICH WE (ALS LABORATORIES) PERFORMED ON HUNDREDS OF SAMPLES FOR ASRD FROM 2011 – 2015. PRESENTED OUR WORK AT AN AMERICAN CHEMICAL SOCIETY MEETING AT UNIVERSITY OF SOUTHERN CALIFORNIA, SAN MARCOS IN 2015.

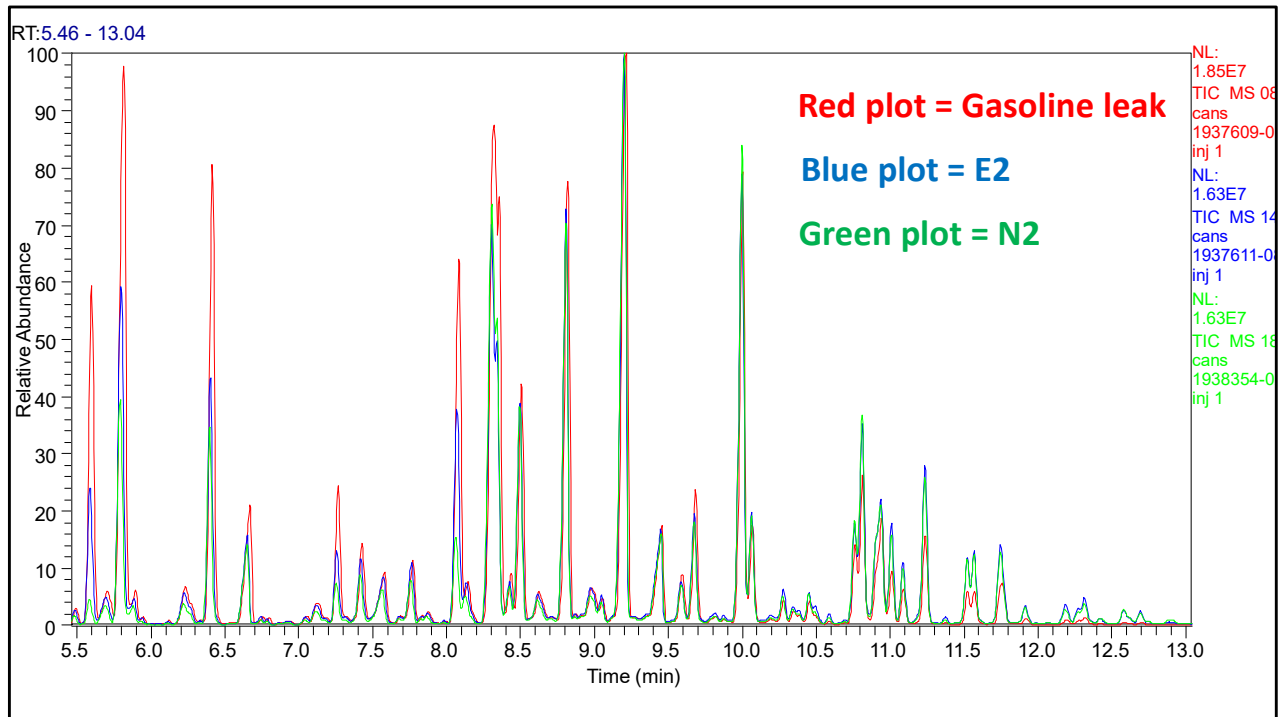




THIS IS A PRICIPAL COMPONENTS ANALYSIS. CLUSTER ANALYSIS (CIRCLES) REVEALED THE SOURCES OF LN (REFERENCE MATERIAL), THE GASOLINE LEAK IS DERIVED FROM A DIFFERENT SOURCE. THE ANALYSIS REVEALS THAT THE 3-PHASE SEPARATOR, E2 AND N2 ARE DERIVED FROM A COMMON SOURCE. HI HAD LITTLE OR NO ALKYLATED BENZENES AND IS THEREFORE NOT INCLUDED.



THIS IS A GC/MS TIC OVERLAY COMPARING THE 3 PHASE SEPARATOR, E2 AND N2. NOTE THE SIMILARITY OF RESPONSE. I.E. CHROMATOGRAMS SUPPORT THE PCA AND CLUSTER ANALYSIS

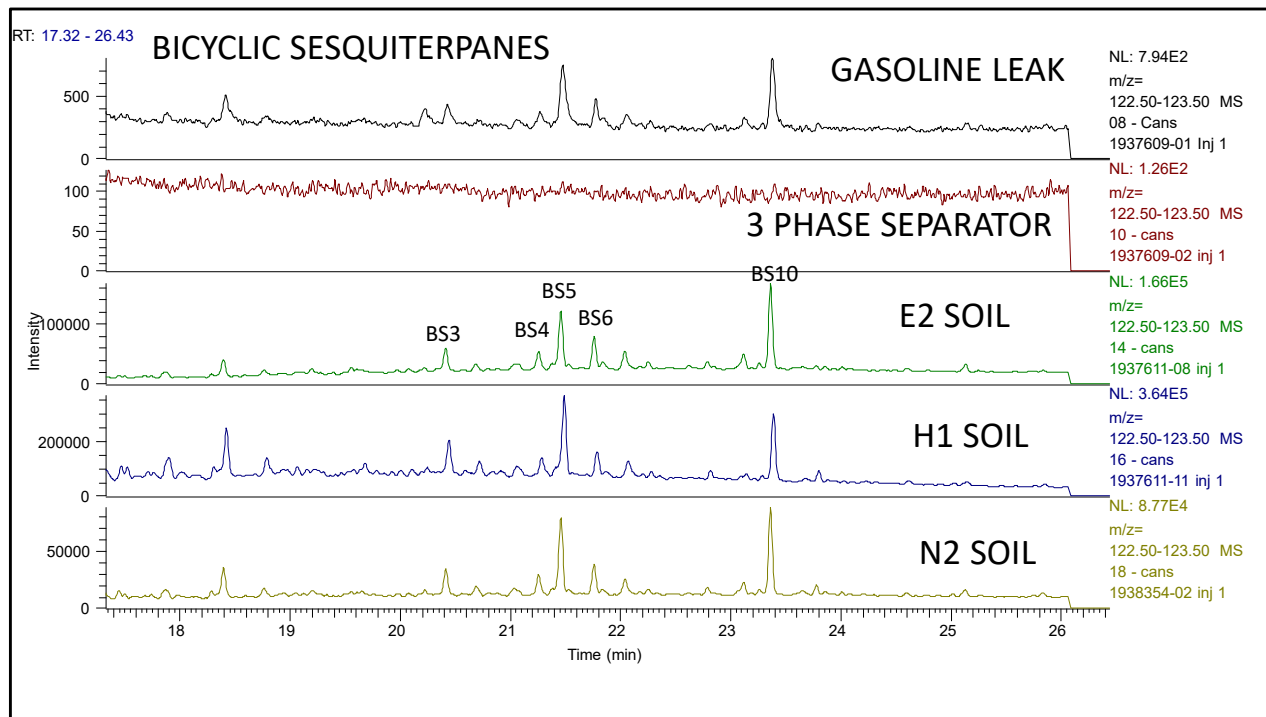


THIS IS A GC/MS TIC CHROMATOGRAPHIC OVERLAY  
 COMPARING THE GASOLINE LEAK, E2 AND N2.  
 ALTHOUGH E2 AND N2 SHOW SIMILARITIES, THE  
 GASOLINE LEAK DOES NOT MATCH. AGAIN SUPPORTING  
 THE PCA AND CLUSTER ANALYSIS

## Preliminary Conclusions using Conventional Chemistry Alone

- Field observations, PHC data, chromatograms and chemometrics suggest that sites E2 and N2 are contaminated with material coming from a source similar to the 3-Phase Separator.
- In other words, current operations could be perceived as being responsible for the contamination observed.
- THIS SUGGESTS LIABILITY BUT IS THIS THE CORRECT CONCLUSION?

THIS SLIDE IS SELF EXPLANATORY



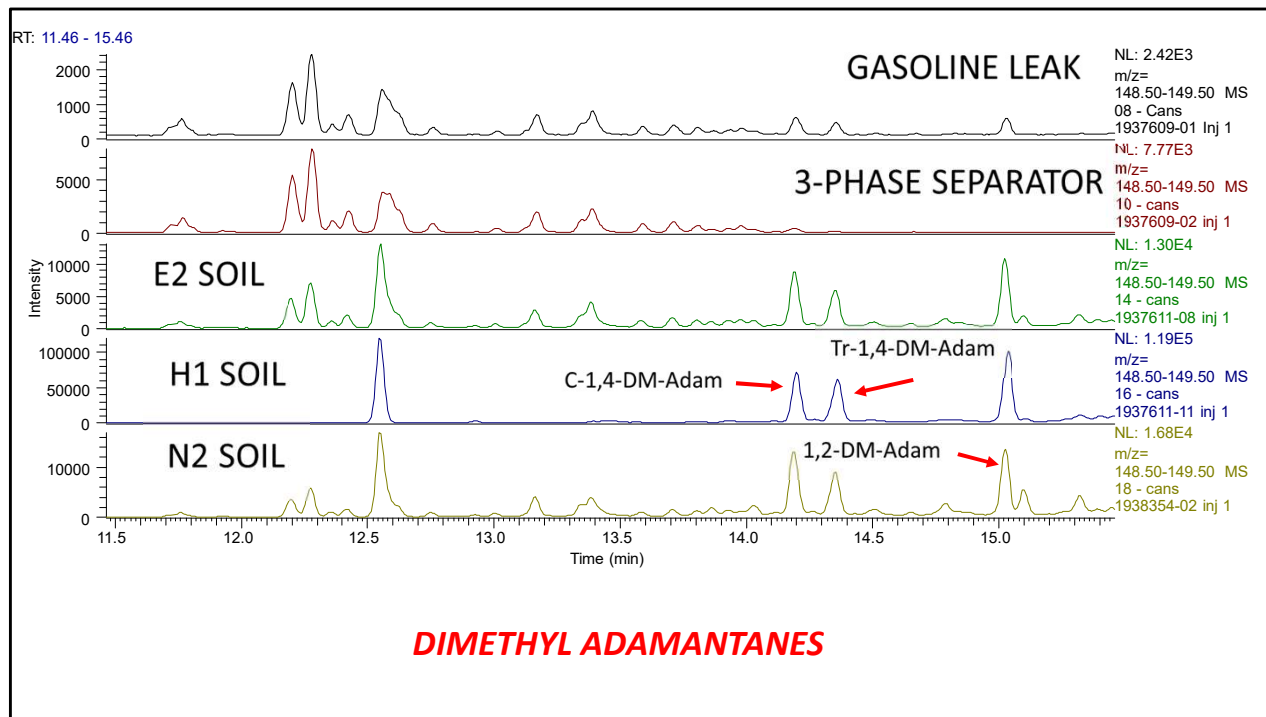
3-PHASE SEPARATOR DOES NOT CONTAIN BICYCLIC SESQUITERPANES. HOWEVER, THE GASOLINE LEAK, E2, H1 AND N2 DO. THIS INFORMATION IS DERIVED USING METHOD EN 15522-2:2023

## *BICYCLIC SESQUITERPANE RATIOS*

Ratio	Gasoline Leak	E2 SOIL	H1 SOIL	N2 Soil
BS4/BS5	0.32	0.32	0.22	0.26
BS5/BS6	2.11	1.78	3.27	2.57
BS3/BS10	0.33	0.27	0.50	0.30
BS4/BS10	0.29	0.22	0.26	0.23
BS5/BS10	0.90	0.68	1.20	0.88
BS6/BS10	0.43	0.38	0.37	0.34

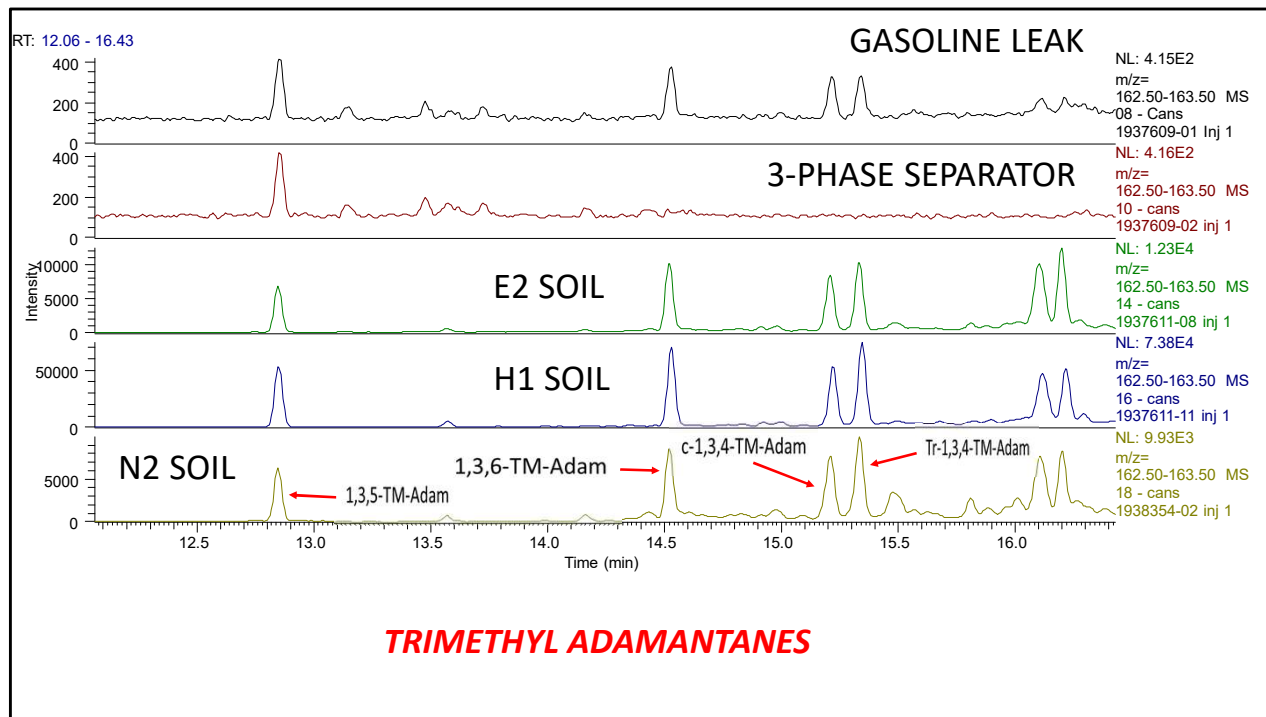
DATA IN GREEN A MATCH USING CRITICAL DIFFERENCE ANALYSIS

COMPARISON OF BICYCLIC SESQUITERPANE RATIOS SHOW THAT THE GASOLINE LEAK, E2, H1, AND N2 ARE NOT RELATED. CONSISTENT WITH PCA ANALYSIS. THE RATIOS ARE SUBJECTED TO A CRITICAL DIFFERENCE ANALYSIS, I.E. THE DIFFERENCE (SOURCE AND SAMPLE)/MEAN \* 100% MUST BE LESS THAN 14% IN ORDER TO DECLARE A MATCH. THIS INFORMATION IS DERIVED USING METHOD EN 15522-2:2023.



DIMETHYL ADAMANTANES ARE OBSERVED TO BE PRESENT IN THE GASOLINE LEAK, E2, H1, AND N2 SAMPLES BUT NOT 3-PHASE SEPARATOR





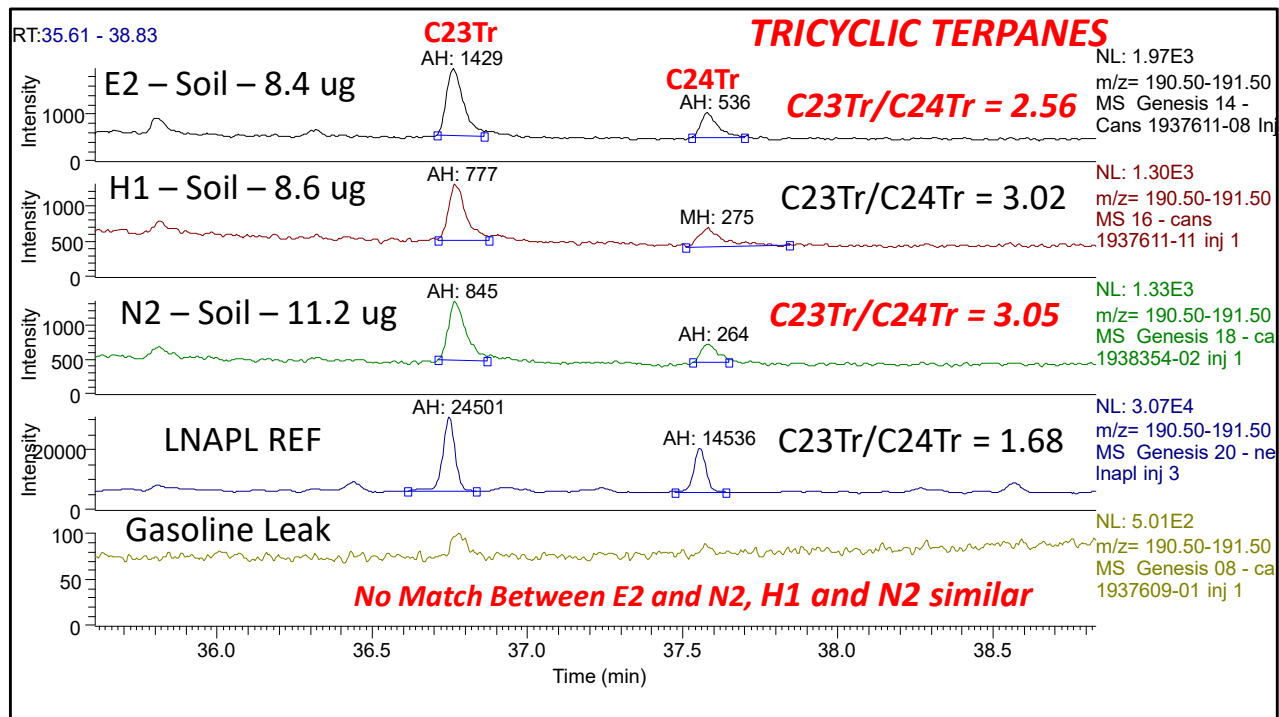
TRIMETHYL ADAMANTANES ARE OBSERVED IN THE GASOLINE LEAK, E2, H1 AND N2 SAMPLES BUT NOT 3-PHASE SEPARATOR.

## *DI- AND TRIMETHYL -ADAMANTANES*

Ratio	Gasoline Leak	E2 SOIL	H1 SOIL	N2 SOIL
C-134-TM-ADAM/Tr-134-TM-ADAM	0.95	0.82	0.72	0.78
135-TM-ADAM/134(C+TR)-TM-ADAM	0.69	0.40	0.43	0.36
136-TM-ADAM/134(C+TR)-TM-ADAM	0.61	0.55	0.55	0.50
135-TM-ADAM-136-TM-ADAM	1.13	0.67	0.78	0.73
C-14-DM-ADAM/TR-14-DM-ADAM	1.44	1.48	1.17	1.50
14(TR+C)-DM-ADAM/12-DM-ADAM	1.89	1.34	1.30	1.61

DATA IN GREEN A MATCH USING CRITICAL DIFFERENCE ANALYSIS

NORMATIVE RATIOS SUGGEST NO COMMON SOURCE FOR THE GASOLINE LEAK, E2, H1, AND N2. OBSERVATION AGREES WITH PCA. NORMATIVE RATIOS MUST BE WITHIN 14% RELATIVE PERCENT DIFFERENCE IF DERIVED FROM A COMMON SOURCE. THIS INFORMATION IS DERIVED USING METHOD EN 15522-2:2023



THIS SLIDE SHOWS THE PRESENCE OF TRICYCLIC TERPANES IN SAMPLES E2, H1, AND N2. PCA/AHC REVEALED THAT E2 AND N2 CAME FROM A COMMON SOURCE. RATIOS INDICATE OTHERWISE BECAUSE RPD IS 17% WHICH EXCEEDS 14% REQUIRED TO BE ASSIGNED TO A COMMON SOURCE. ALTHOUGH RATIOS FOR H1 AND N2 MATCH, WE KNOW FROM THE CHROMATOGRAM THAT THESE SAMPLES ARE DERIVED FROM A DIFFERING SOURCE

## Weathering Assessment: Evaporation

- Evaporation is the most significant weathering effect following release of light petroleum products such as gasoline and condensate
- Ratios assessing evaporation from gasoline include (Stout et al., 2006):
  - n-pentane/n-heptane (C<sub>5</sub>H<sub>12</sub> / C<sub>7</sub>H<sub>16</sub>)
  - 2-methylpentane/2-methylheptane (C<sub>6</sub>H<sub>14</sub>/C<sub>8</sub>H<sub>18</sub>)
  - Isopentane/n-heptane (C<sub>5</sub>H<sub>12</sub>/C<sub>7</sub>H<sub>16</sub>)
  - n-heptane/n-decane (C<sub>5</sub>H<sub>12</sub>/C<sub>10</sub>H<sub>22</sub>)
- EN 2023 normalizes all biomarkers to bicyclic sesquiterpane 10 (BS 10), phytane or hopane in order to assess weathering. We employed BS10
- In this study bicyclic sesquiterpanes (BS-1, -2, 3, -4, -5, -6, -8, -9, and 10) were detected (C<sub>14</sub>H<sub>26</sub>, C<sub>15</sub>H<sub>28</sub>, C<sub>16</sub>H<sub>30</sub>)
- Also detected were dimethyl- and trimethyl-adamantanes (C<sub>12</sub>H<sub>20</sub> and C<sub>13</sub>H<sub>22</sub>)
- Bicyclic sesquiterpanes and adamantanes are stable to biodegradation but can be affected by evaporation. Using BS10 is a much better option for assessing evaporation of samples than those parameters identified in the literature.
- Also, the samples are more like condensate and middle distillates therefore use of gasoline weathering indices is inappropriate.

THIS SLIDE IS SELF EXPLANATORY

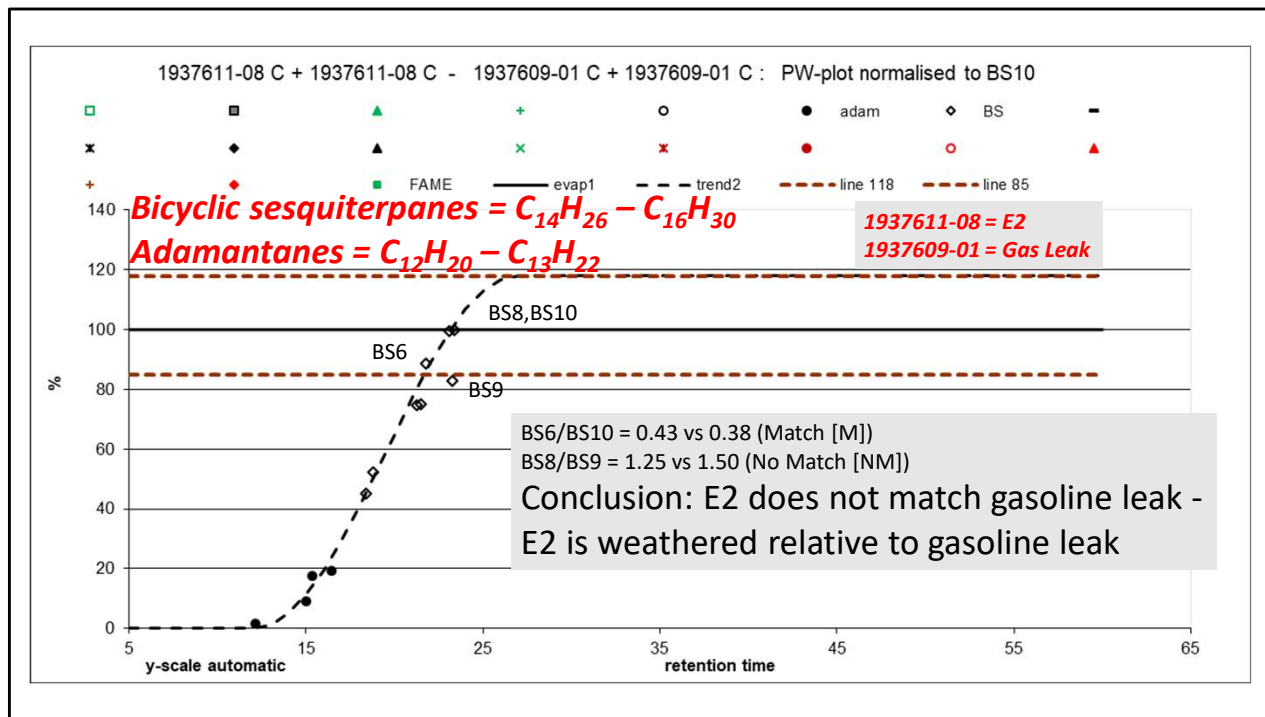
## Percent Weathering (PW) CALCULATIONS

$$\%C_{\text{NSPILL}} = C_{\text{NSPILL}}/C_{\text{BS10SPILL}} // C_{\text{NSOURCE}}/C_{\text{BS10SOURCE}}$$

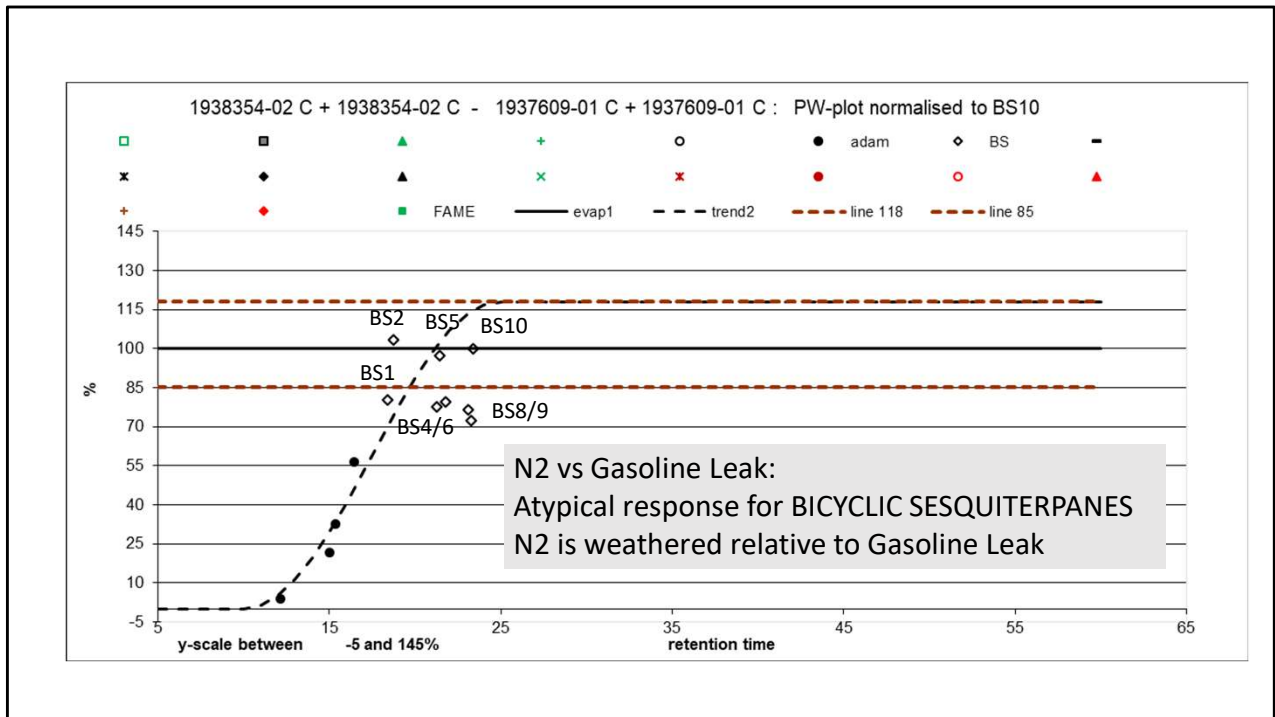
**EXAMPLE**

$$\%BS6_{\text{SPILL}} = C_{\text{BS6SPILL}}/C_{\text{BS10SPILL}} // C_{\text{BS6SOURCE}}/C_{\text{BS10SOURCE}}$$

THIS SLIDE SHOWS HOW GAS CHROMATOGRAPHY/MASS SPECTROMETRY PERCENT WEATHERING PLOTS (GC/MS PW PLOTS) ARE GENERATED, I.E. THE RELATIONSHIP OF ONE PARTICULAR BIOMARKER TO EACH SAMPLE TESTED. NOTE ALL BIOMARKERS ARE NORMALIZED TO BS 10. THIS PROCESS IS DERIVED FROM METHOD EN 15522-2:2023

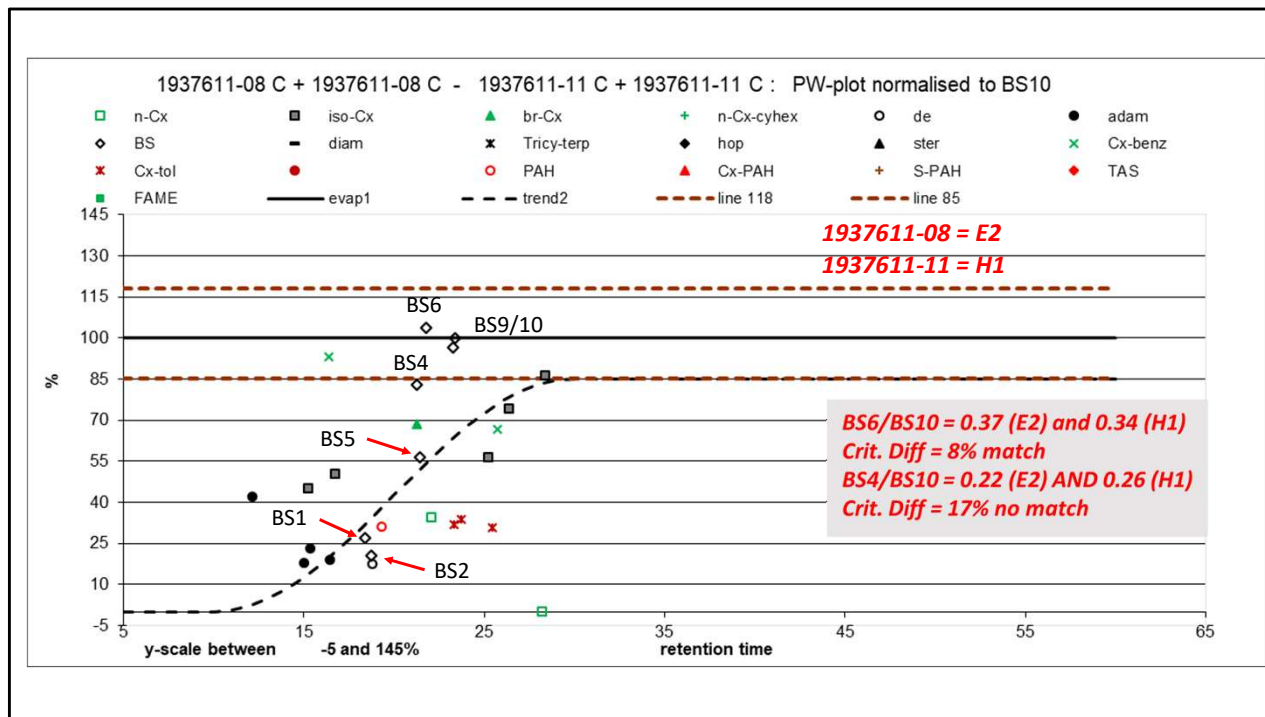


GC/MS PERCENT WEATHERING PLOT COMPARING 1937611-08 (E2) AND 1937609-01 (Gas Leak). ADAMANTANES AND BICYCLIC SESQUITERPANES ARE VERY STABLE. REDUCTIONS SUGGEST EVAPORATION. REDUCED LEVELS OF ADAMANTANES OBSERVED IN E2 BECAUSE OF EVAPORATION. NOTE ALIGNMENT WITH EVAPORATION LINE. SUPPORTS WEATHERING OF E2 OVER GAS LEAK. SUGGESTS THAT GASOLINE LEAK IS MORE RECENT SPILL MATERIAL AND THAT E2 IS FROM A HISTORIC SPILL.

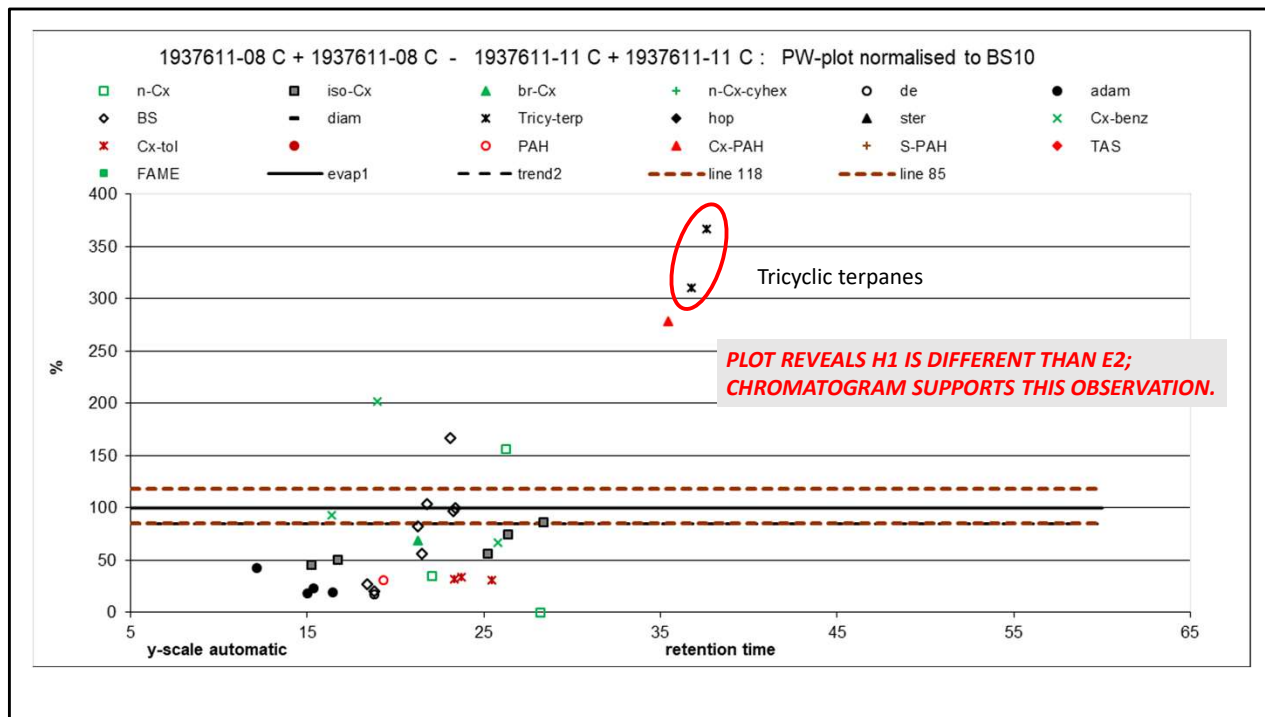


COMPARISON OF 1938534-02 (N2) VS 1937609-01 (Gas Leak). NOTE ADAMANTANES ARE WEATHERED IN N2. SUPPORTS DATA TO SHOW THAT N2 IS FROM A HISTORIC SPILL. WEATHERING OF BICYCLIC SESQUITERPANES IS UNUSUAL. HIGHER MW BICYCLIC SESQUITERPANES EVAPORATED MORE THAN LOW MW. E.G BS5 (MW 208) AND BS8/9 (MW 222). THIS MAKES NO SENSE. THIS OBSERVATIOIS SUGGESTS DIFFERING SOURCES

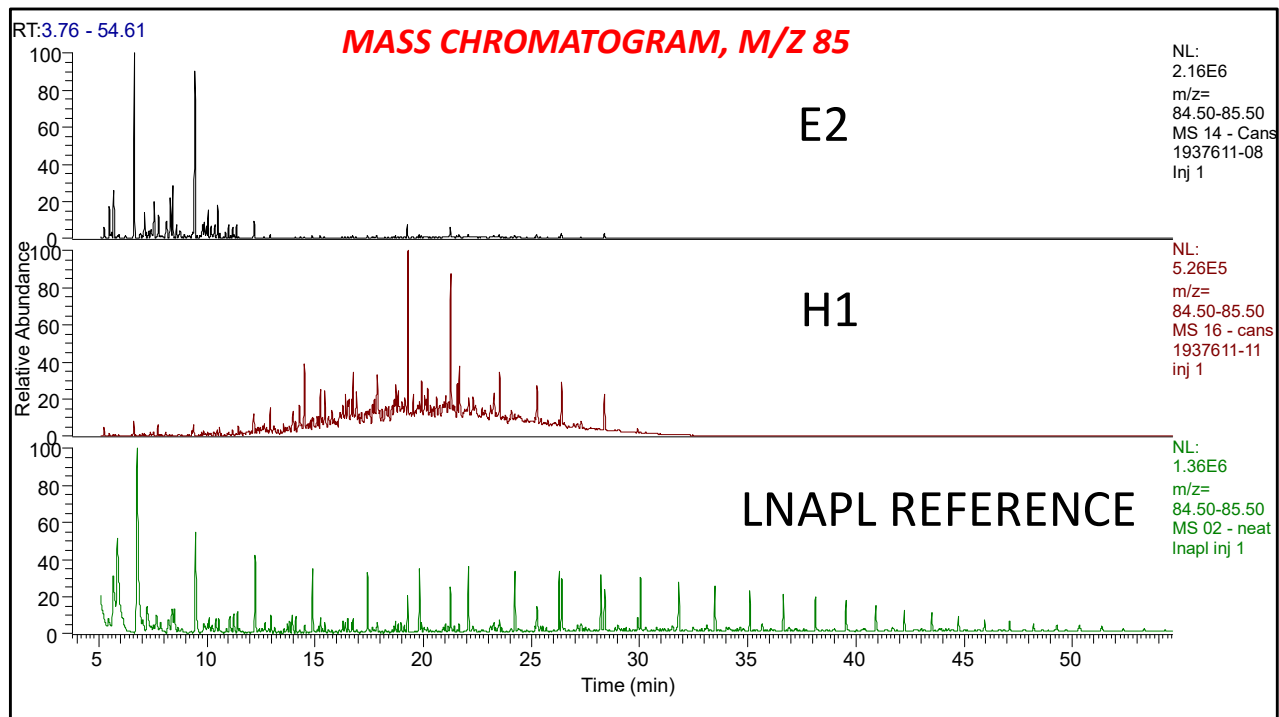




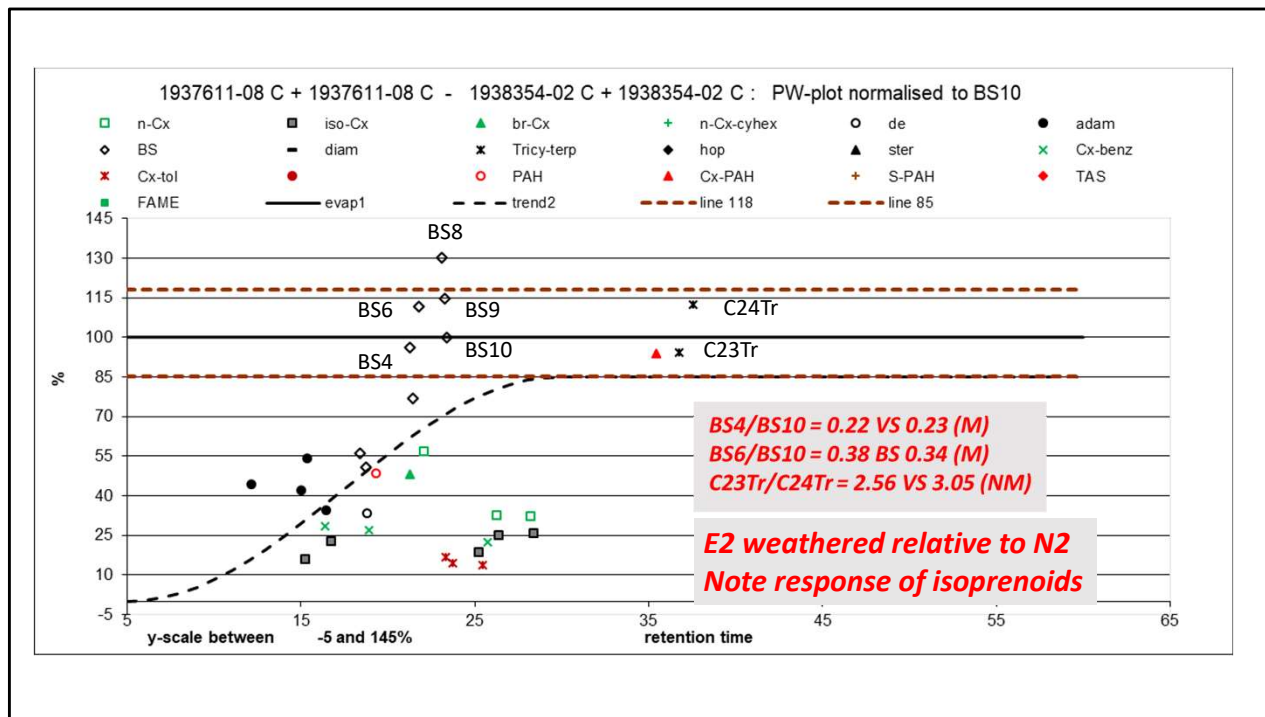
THIS IS A GC/MS WEATHERING PLOT COMPARING 1937611-08 (E2) WITH 1937611-11 (H1). NOTE THE WEATHERING PATTERN IS ATYPICAL OF WHAT WE EXPECT, I.E. ADAMANTANES DO NOT FOLLOW THE EVAPORATION LINE. DISTRIBUTION REFLECTS DIFFERING SOURCES. ALSO RATIOS OF BICYCLIC SESQUITERPANES ERRATIC, BS6/BS10 PASSES AND BS4/BS10 DOES NOT.



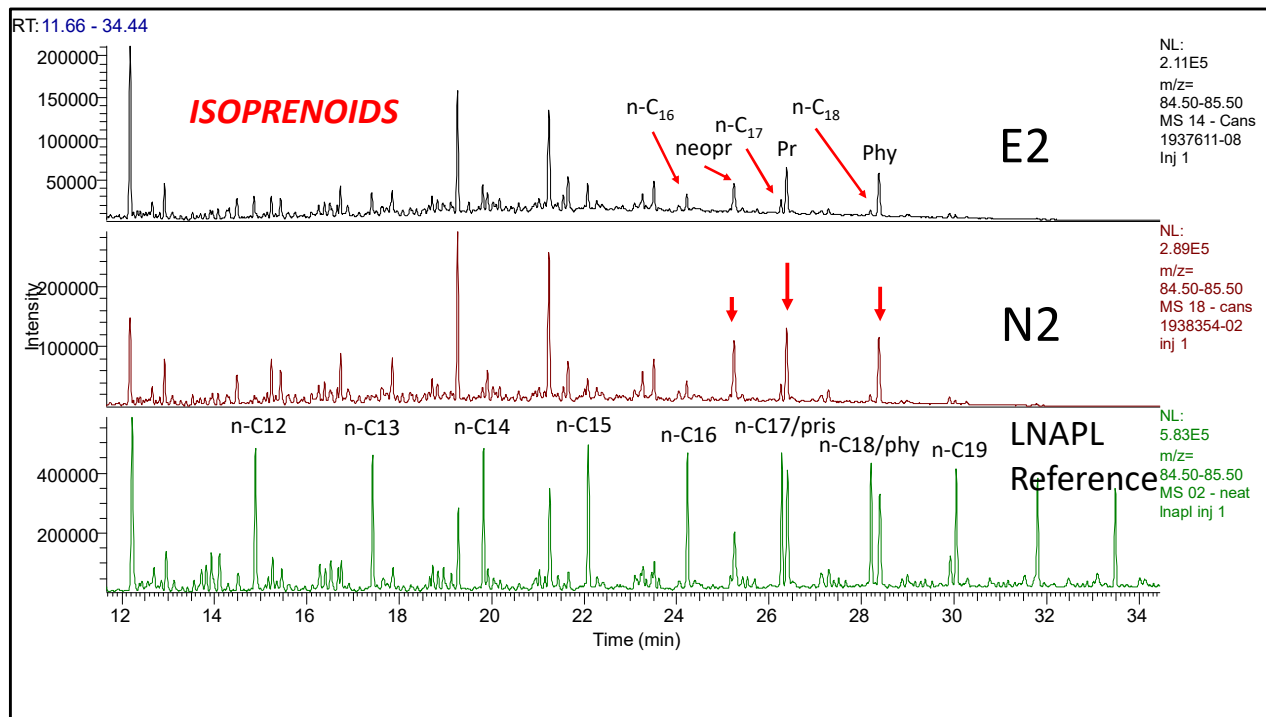
THIS IS A GC/MS PW PLOT COMPARING E2 AND H1. NOTE THE HIGHER LEVELS OF TRICYCLIC TERPANES IN H1 INDICATING MORE MIDDLE DISTILLATE



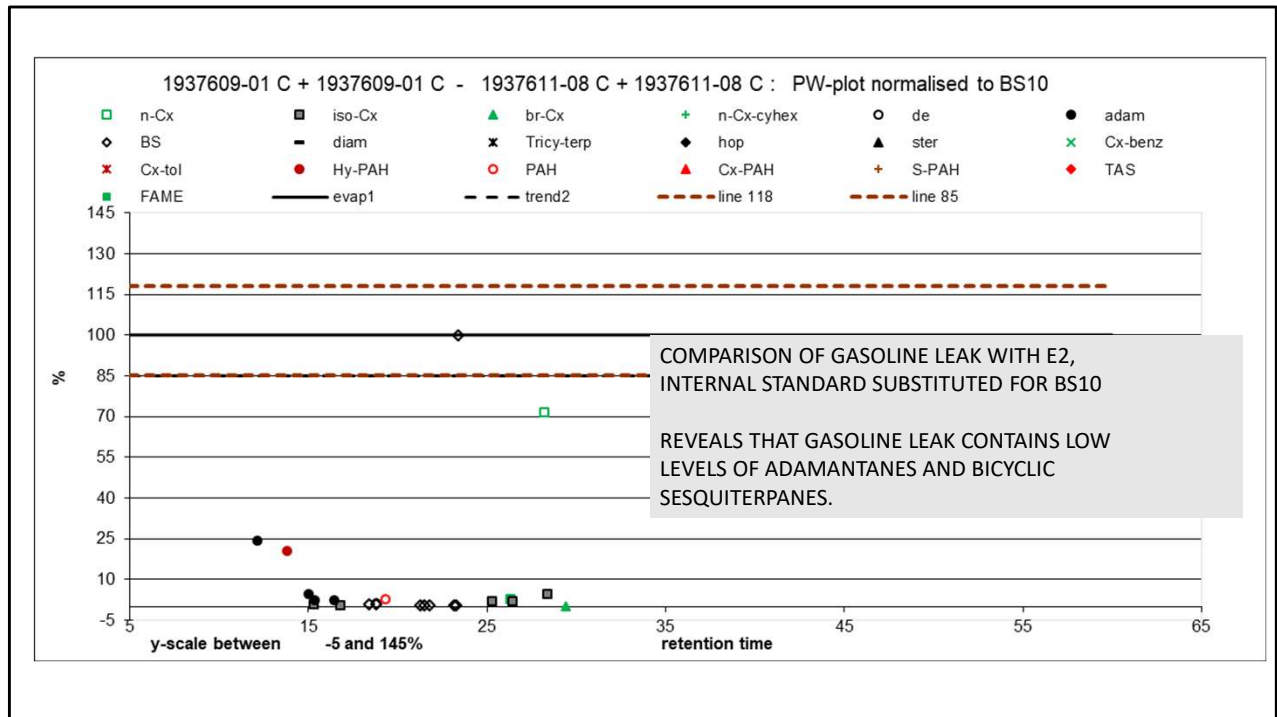
THIS AN EXTRACTED ION-CURRENT PROFILE FOR M/Z 85 CHARACTERISTIC OF n-ALKANES AND ISOPRENOIDS. NOTE THE DIFFERENCE BETWEEN H1 AND E2 INDICATING DISSIMILAR PRODUCTS. CHROMATOGRAM FOR H1 EXPANDS TO PHYTANE, INDICATING THIS SAMPLE IS LIKELY A WEATHERED MIDDLE DISTILLATE, NOT STRAGHT RUN GASOLINE.



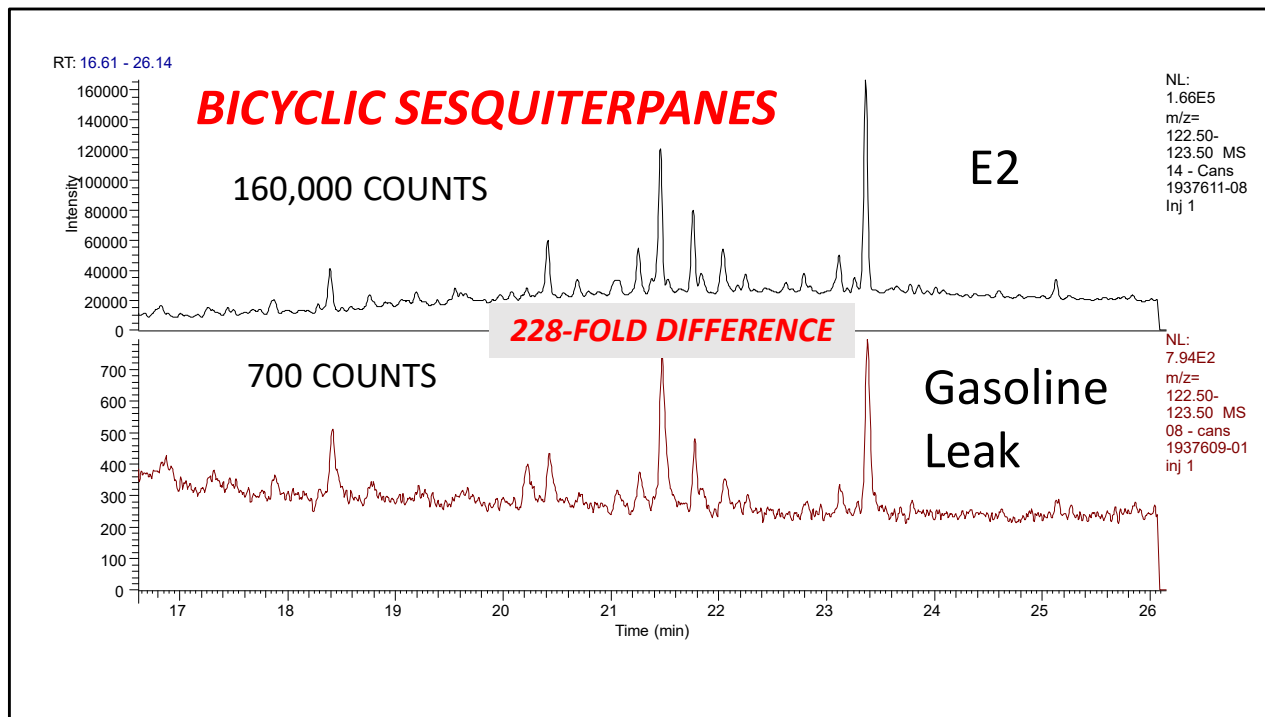
THIS IS A WEATHERING PLOT COMPARING 1937611-08 (E2) AND 1938354-02 (N2). FROM THIS PLOT IT APPEARS THAT E2 IS WEATHERED RELATIVE TO N2 INDICATING THAT PETROLEUM IN THESE SITES WERE RELEASED AT DIFFERING TIMES. ALTHOUGH THE BICYCLIC SESQUITERPANE RATIOS MATCH MORE STABLE TRICYCLIC TERPANES RATIOS DO NOT MATCH. THESE OBSERVATIONS SUGGEST DIFFERING SOURCES FOR E2 AND N2.



THIS IS MASS CHROMATOGRAM FOR M/Z 85 CHARACTERISTIC OF n-ALKANES AND ISOPRENOIDS. BOTH ARE COMPARED TO A MIXTURE OF CONDENSATE AND CRUDE OIL. NOTE BOTH E2 AND N2 ARE BIODEGRADED RELATIVE TO OUR REFERENCE MIXTURE INDICATING THAT THESE WERE RELEASED AT DIFFERING TIMES.



THIS IS A GC/MS PW PLOT COMPARING THE GASOLINE LEAK SAMPLE WITH E2. DATA IS NORMALIZED TO OUR INTERNAL STANDARD BECAUSE BS10 WAS NOT PRESENT IN BOTH SAMPLES. THE GASOLINE LEAK CONTAINS LOWER LEVELS OF ADAMANTANES AND BICYCLIC SESQUITERPANES THAN E2 INDICATING A LIGHTER PETROLEUM PRODUCT



THIS SLIDE SHOWS A GC/MS EXTRACTED ION-CURRENT PROFILE FOR M/Z 123, WHICH IS CHARACTERISTIC OF BICYCLIC SESQUITERPANES. TOTAL ION COUNTS (INTENSITY) CONFIRMS MUCH LOWER RESPONSES OF BICYCLIC SESQUITERPANES IN THE GASOLINE LEAK SAMPLE, I.E. 228-FOLD LOWER RESPONSE.

# QUALITY CONTROL

SEVERAL QUALITY CONTROL MEASURES ARE AN INTEGRAL PART OF METHOD EN 15522-2:2023

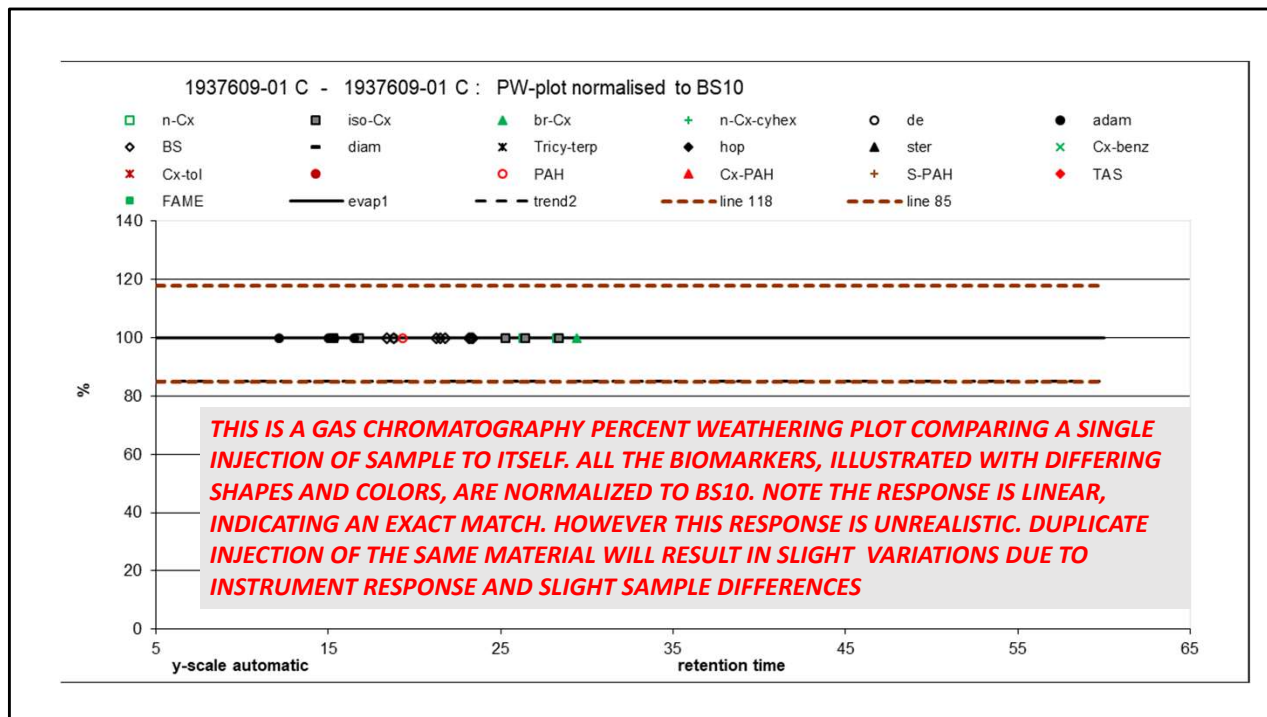


## PERCENT WEATHERING PLOT: DUPLICATE ANALYSES

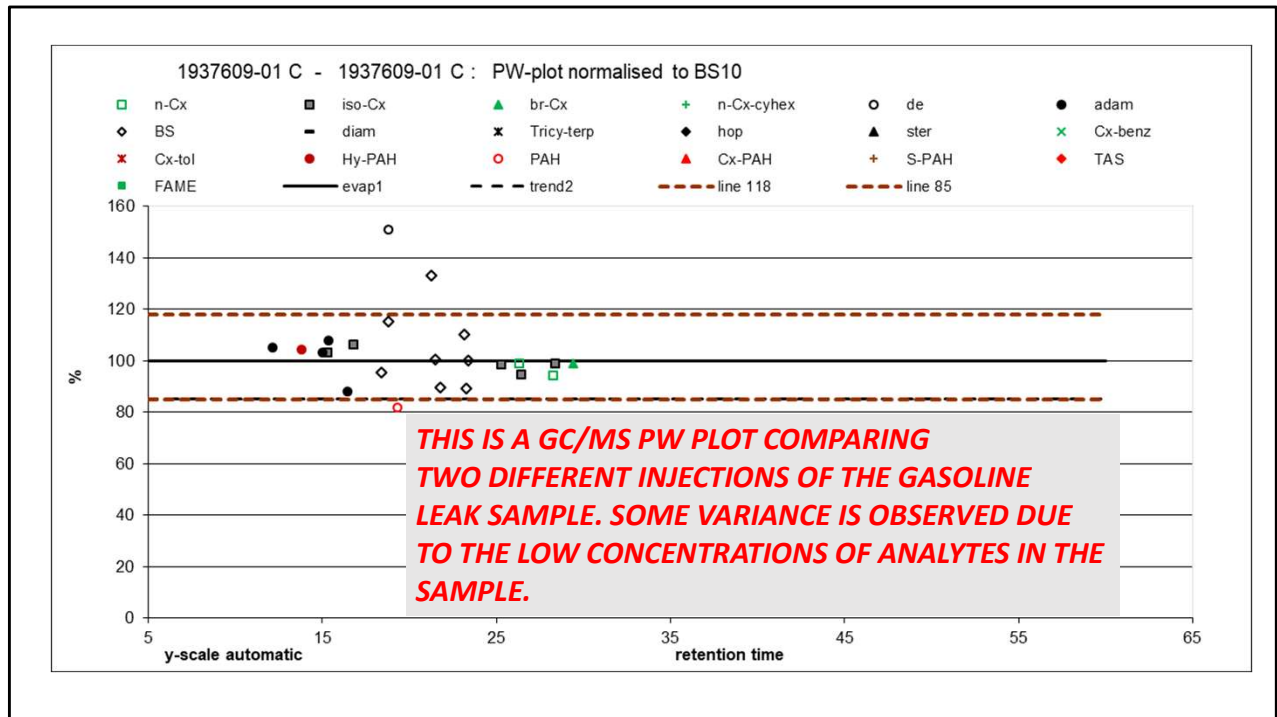
$$\%C_{\text{NSPILL}} = C_{\text{N-INJ1}}/C_{\text{BS10-INJ1}} // C_{\text{N-INJ2}}/C_{\text{BS10-INJ2}}$$

**EXAMPLE**

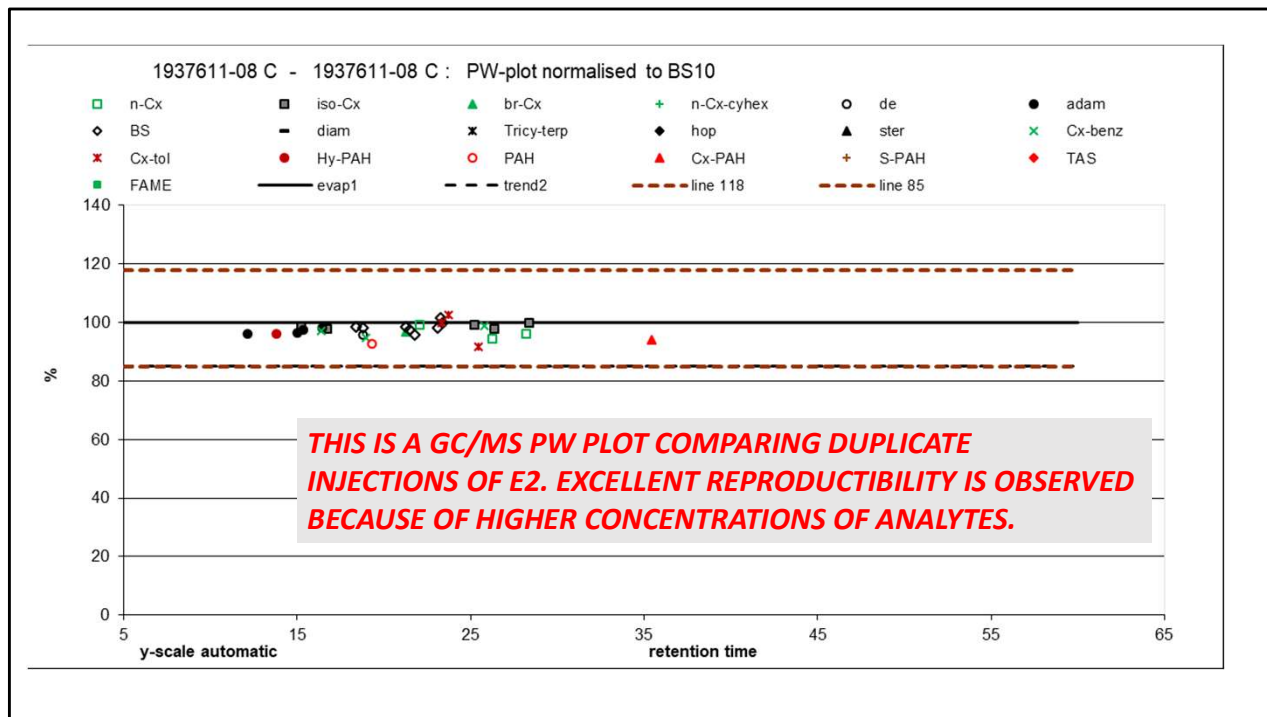
$$\%BS6_{\text{SPILL}} = C_{\text{BS6-INJ1}}/C_{\text{BS10-INJ1}} // C_{\text{BS6-INJ2}}/C_{\text{BS10-INJ2}}$$



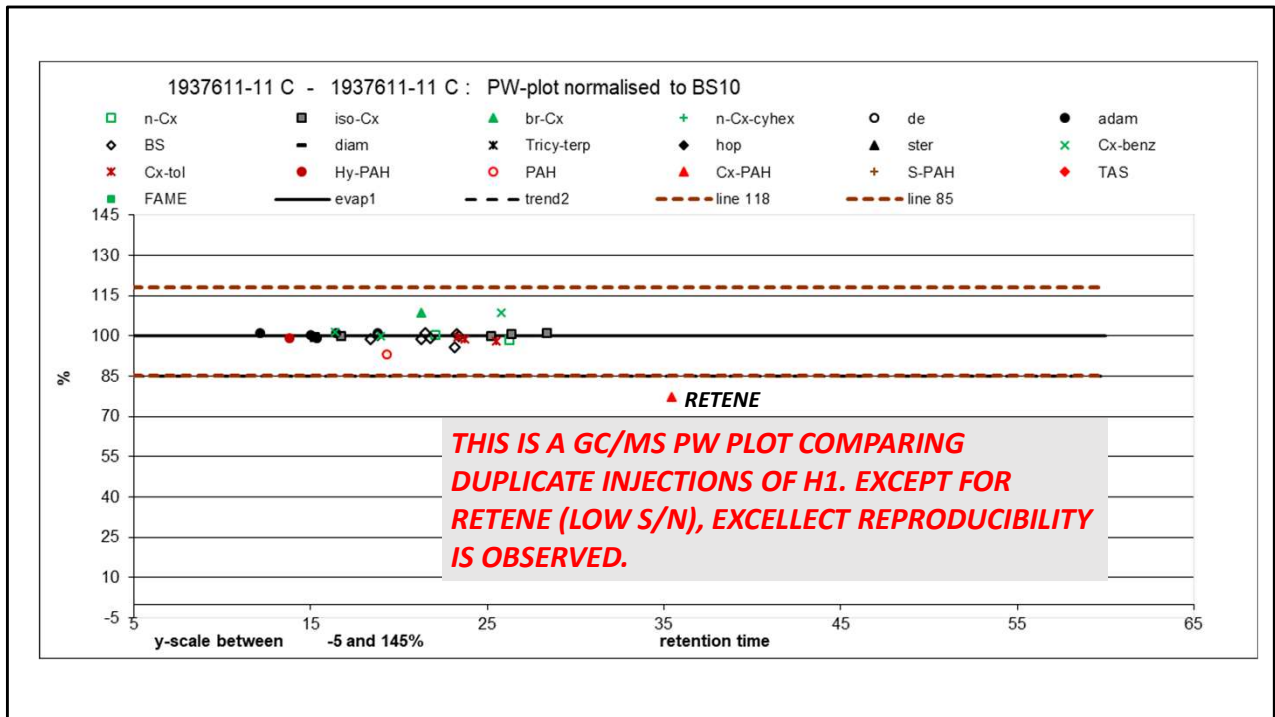
SLIDE IS SELF EXPLANATORY



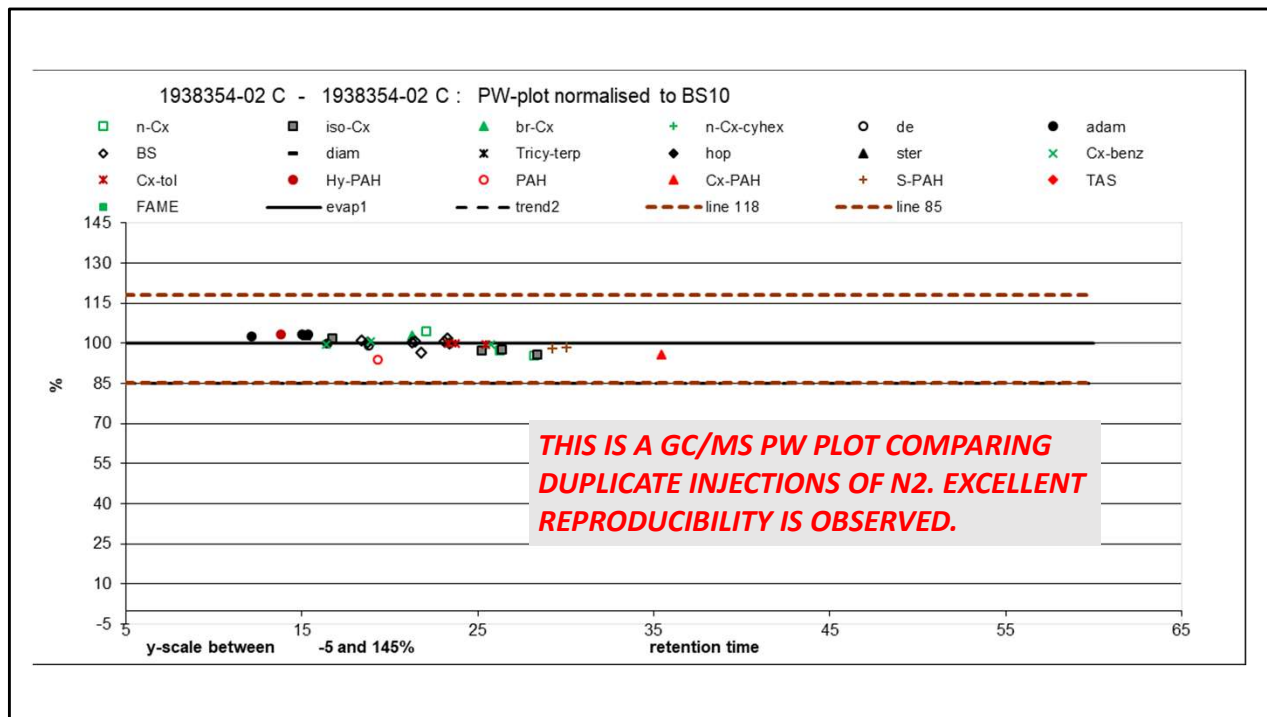
DUPLICATE ANALYSIS OF GASOLINE LEAK. SOME SCATTER OBSERVED DUE TO LOW LEVELS OF ANALYTES



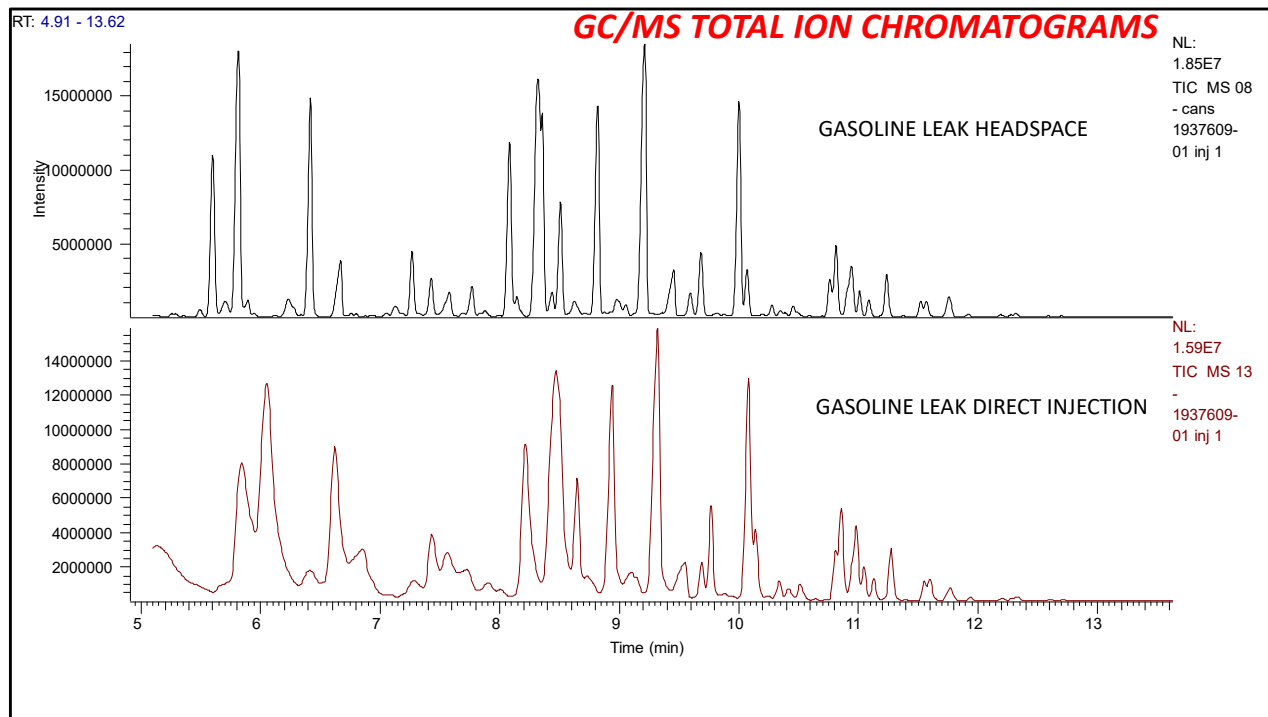
DUPLICATE ANALYSIS OF E2. EXCELLENT REPRODUCIBILITY



DUPLICATE ANALYSIS OF H1 EXCELLENT REPRODUCIBILITY



DUPLICATE ANALYSIS OF N2 EXCELLENT REPRODUCIBILITY



THIS IS A COMPARISON OF THE GASOLINE LEAK SAMPLE ANALYZED USING HEADSPACE AND DIRECT INJECTION ANALYSIS. A SIMILAR RESPONSE IS OBSERVED.

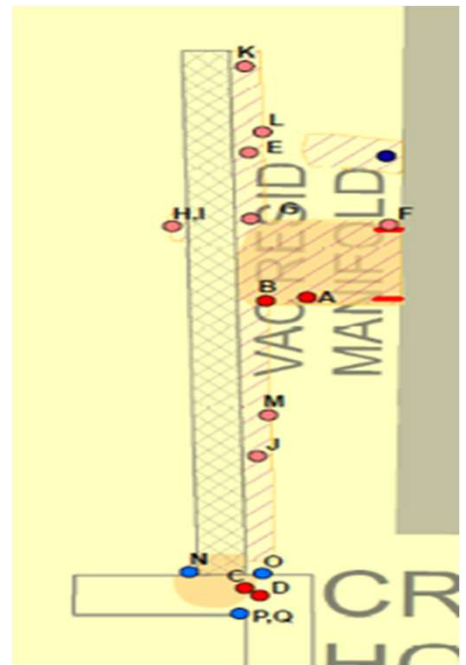
Sample Identification	Percent Naphthalene-D8 Recovery
injection 1 GAS LEAK	51
injection 2 GAS LEAK	51
injection 1 PHASE 3/SEP	36
injection 2 PHASE 3/SEP	34
injection 1 E2	49
injection 2 E2	48
injection 1 H1	58
injection 2 H1	58
injection 1 N2	50
injection 2 N2	50

RECOVERIES FOR SURROGATE SIMILAR FOR GAS LEAK, E2, H1, AND N2. RELATIVE STANDARD DEVIATION (RSD) IS 7.5%. HI IS HIGHLY WEATHERED. COMPARING GAS LEAK, E2, AND N2 THE CONSISTENCY IN RESPONSE IS EXCELLENT WITH A RSD OF 2.3%



## CONCLUSIONS

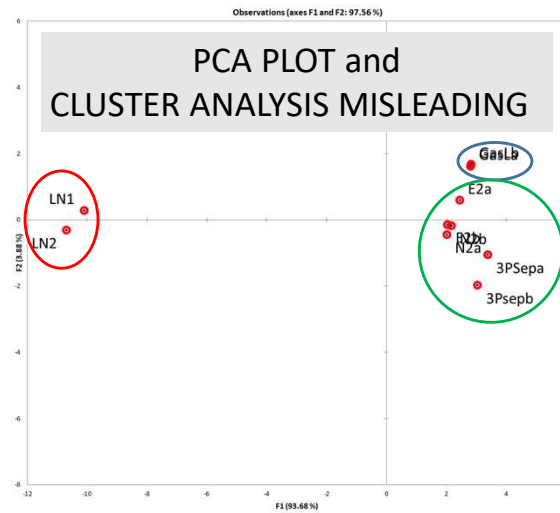
- N2 AND E2 ARE NOT DERIVED FROM PHASE 3 SEPARATOR AS PREDICTED BY PRINCIPAL COMPONENTS ANALYSIS (PCA)
- N2 AND E2 ARE NOT DERIVED FROM A COMMON SOURCE. DIFFERING WEATHERING PROFILES INDICATE DIFFERING TIMES OF RELEASE AND RATIOS INDICATE DIFFERING SOURCES.
- THE GASOLINE LEAK MAY BE CONTAMINATED WITH HISTORIC SPILL MATERIAL (A). IT MAY BE A DIFFERENT CRUDE OIL STOCK AS WELL. HOWEVER, THE PCA AND CHROMATOGRAMS INDICATE A DIFFERENT SOURCE THAN THE PHASE 3 SEPARATOR GAS SAMPLE.

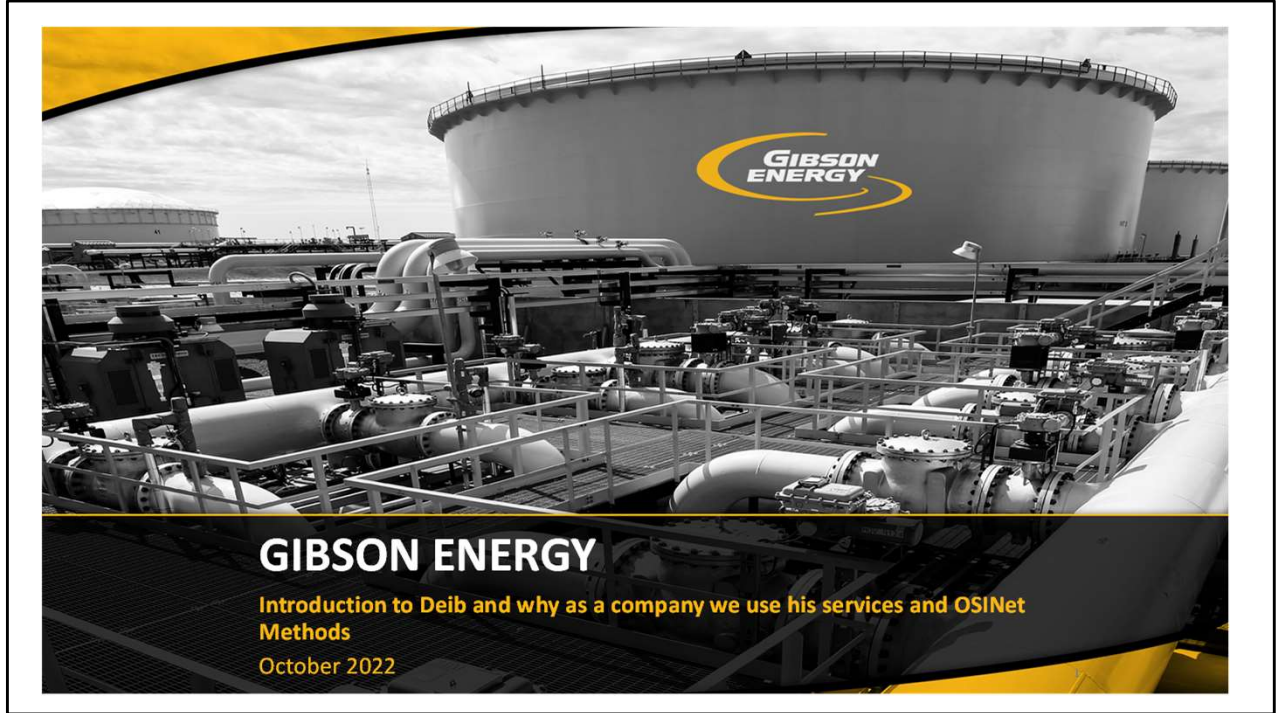


SELF EXPLANATORY

# CONCLUSIONS

- PRINCIPAL COMPONENTS ANALYSIS IS A USEFUL TOOL BUT NOT DEFINITIVE FOR DEFINING SPILL AND SOURCE RELATIONSHIPS, ESPECIALLY IF USED IN LITIGATION.
- DETERMINING HYDROCARBON RATIOS IS HIGHLY RECOMMENDED BUT WHICH ONES DO YOU CHOOSE ? THOSE DEFINED BY THE LITERATURE? THOSE DEFINED BY EN2023?
- ALSO, RATIOS CAN BE AFFECTED BY WEATHERING – HOW DO YOU DETERMINE THAT? THROUGH THE LITERATURE OR METHOD EN2023?
- IF INAPPROPRIATE RATIOS ARE EMPLOYED IN PCA THEN THE CONCLUSIONS MAY BE ERRONEOUS
- EN2023 PRESCRIBES CHEMICALS TO MEASURE AND RATIOS TO FOCUS ON, BASED UPON **DIAGNOSTIC POWER**.
- EN2023 PRESCRIBES WEATHERING PROCEDURES BY NORMALIZING DATA TO BS10, PHYTANE AND/OR HOPANE.





## **GIBSON ENERGY**

**Introduction to Deib and why as a company we use his services and OSINet  
Methods**  
October 2022

# OPENING REMARKS BY GIBSON ENERGY

## Need For Forensic Fingerprinting – Proponents Angle

- Too often we have uncertainty over ownership and responsibility of liabilities for sites where multiple companies have historical facilities
- We need a defensible and accepted methodology differentiation / forensic fingerprinting to ascertain this ownership
- We use Deib consistently in circumstances like this due to his 40+ year expertise in analytical chemistry & forensics and because he is a leading proponent of the Oil Spill Identification Network of experts (OSINet) methods which were developed in the aftermath of the Tricolor spill in the English Channel in 2002 under the Bonn agreement have international recognized fingerprinting protocols
- We believe that this now recognized international methodology to differentiate sources will hold up in courts and eventually cascade from marine acceptance to land locked prairie regulatory acceptance
- **We thank Deib for his expertise and for spearheading these methods into the western Canadian oil patch**

49

# OPENING REMARKS GIBSON ENERGY

**Detlef (Deib) Birkholz**

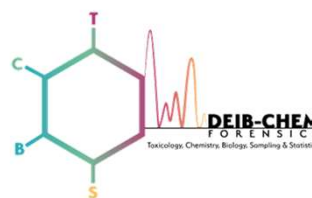
MSc., PhD., P. Chem.  
Edmonton, Alberta

website: <https://deib-chemforensics.com>

Email: [birkholz@deib-chemforensics.com](mailto:birkholz@deib-chemforensics.com)

Phone: 587-597-5197

Forensic services in toxicology (T), chemistry (C)  
biology (B), sampling and statistics (S)



# CONTACT INFORMATION